Engin. Library

SEP - 4 1935

Vol. 21 AUGUST, 1935 No. 142

JOURNAL OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

FOUNDED 1913—INCORPORATED 1914

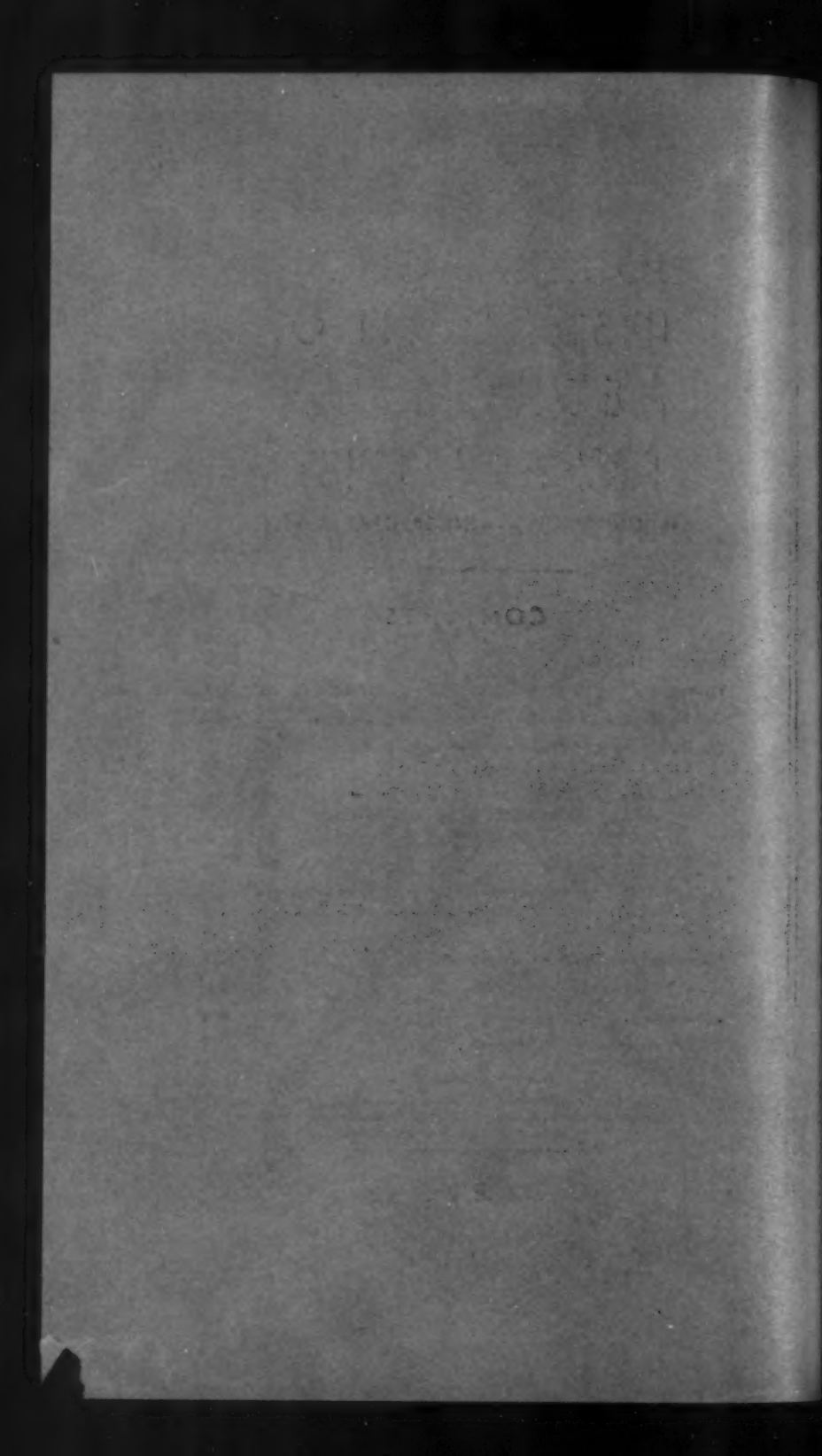
CONTENTS

	PAGE
Institution Notices	i–viii
Viscosity and Thixotropy of Drilling Mud. P. Evans and A. Reid	677
One Hundred and Sixty-fifth General Meeting	680
The Development of Wire Rope Pumping in Rumania. Percy R. Clark and Lutz F. W. Schropp	691
Improved Method of Examining Mineral Oils, Especially the High-Boiling Components. H. J. C. Vlugter, H. I. Waterman and H. A. van Westen	701
The Refining of a Cracked Motor Spirit. D. Glynn Jones, M.Sc.	709
Two Methods for the Estimation of the Porosity of Limestone. W. H. Thomas, A.R.S.M., R. A. E. Chisholm, B.Sc., and A. B. Cameron, B.Sc.	725
Bibliography on Oil-Well Cement. A. Reid	734
Gas-Oil Separators. J. W. Hardy	741
Abstracts	285a
Book Reviews and Books Received	318a

Published by The Institution of Petroleum Technologists, Aldine House, Bedford Street, Strand, London, W.C. 2, and Printed in Great Britain by R. Clay & Sons, Ltd., Bungay, Suffolk.

PRICE 7s. 6d.

All rights of Publication or Translation are reserved.



THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

List of Officers, 1935–1936.

Past-Presidents :

*Sir Boverton Redwood, Bart., D.Sc., F.R.S.E. (1914–1916).
Prof. Sir John Cadman, G.C.M.G., D.Sc., Hon. LL.D., Hon.D.Eng. (1916–1917).
*The Rt. Hon. Lord Greenway of Stanbridge Earls (1917–1919).
*Sir Frederick W. Black, K.C.B., B.A. (Lond.) (1919–1921).
Prof. John Samuel Strafford Brame, C.B.E., F.I.C., F.C.S. (1921–1923).
*Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng. (1923–1925).
Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (1925–1927).
Alfred C. Adams (1927–1929).
A. E. Dunstan, D.Sc., F.I.C., F.C.S. (1929–1931).
James Kewley, M.A., F.I.C., F.C.S., M.I.Chem.E. (1931–1933).
T. Dewhurst, A.R.C.Sc., F.G.S. (1933–1935).

President :

Prof. Sir John Cadman, G.C.M.G., D.Sc., Hon. LL.D., Hon.D.Eng.

Vice-Presidents :

Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.
Ashley Carter, A.M.I.Mech.E.
C. Dalley, M.I.E.E.
Prof. A. W. Nash, M.Sc., F.C.S., M.I.Mech.E.
J. McConnell Sanders, F.I.C., F.C.S.
F. B. Thole, D.Sc., F.I.C., F.C.S.

Members of Council :

G. H. Coxon.
A. Frank Dabell, M.I.Mech.E.
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.
Elliott A. Evans, F.C.S.
F. H. Garner, Ph.D., M.Sc., F.I.C.
T. R. H. Garrett, M.A., F.G.S.
W. E. Gooday, A.R.S.M., D.I.C., M.Inst.M.M.
A. C. Hartley, A.C.G.I., M.Inst.C.E., M.I.Mech.E.
Prof. V. C. Illing, M.A., M.Inst.M.M.
J. S. Jackson, B.Sc., A.I.C.
E. R. Redgrove, Ph.D., B.Sc., F.C.S.
James Romanes, M.A., F.G.S.
A. Beeby Thompson, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S.
A. Wade, D.Sc., A.R.C.S., F.G.S., M.Inst.M.M., F.Am.G.S.
Cecil W. Wood, F.I.C.

* Deceased.

Chairmen of Committees of Council :

Awards : The President.
Benevolent Fund : A. E. Dunstan, D.Sc., F.I.C., F.C.S.
Branch : T. Dewhurst, A.R.C.Sc., F.G.S.
Cancer Research : J. Kewley, M.A., F.I.C., F.C.S., M.I.Chem.E.
Chemical Standardization : Prof. J. S. S. Brame, C.B.E., F.I.C., F.C.S.
Election : J. McConnell Sanders, F.I.C., F.C.S.
Engineering Standardization : Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.
Finance : C. Dalley, M.I.E.E.
House : Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.
Library : James Romanes, M.A., F.G.S.
Publication : A. E. Dunstan, D.Sc., F.I.C., F.C.S.
Research Fund : J. Kewley, M.A., F.I.C., F.C.S., M.I.Chem.E.

Chairmen of Branches :

Persia : E. C. Brewster.
Rumania : P. R. Clark.
Trinidad : Commander H. V. Lavington, R.N.
South Wales : W. C. Mitchell, B.Sc., M.Inst.C.E., M.I.Mech.E
Burma : G. W. Lepper, B.Sc., F.G.S.

Chairmen of Students Section :

London Branch : A. S. Bridgwater.
Birmingham Branch : E. R. Ward.

Honorary Treasurer :
Lord Plender of Sundridge, G.B.E.

Solicitors :
Messrs. Ashurst, Morris, Crisp & Co.

Auditors :
Messrs. Price, Waterhouse & Co.

Bankers :
Westminster Bank, Limited.
21, Lombard Street, London, E.C. 3.

Hon. Editor :
A. E. Dunstan, D.Sc., F.I.C., F.C.S.

Associate Editor, Librarian and Secretary, Standardization Committee :
George Sell.

Hon. Secretary :
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.

Secretary :
S. J. Astbury, M.A., A.M.Inst.C.E

Offices—Aldine House, Bedford Street, Strand, London, W.C. 2.
Telegrams : Instpetech, Lesquare, London.
Telephone : Temple Bar 1842.

NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright.—Publication of abstracts of Papers and articles appearing in the Journal is permitted, provided that acknowledgment is made to the Institution of Petroleum Technologists.

Papers and Articles.—The Council invites Papers and Articles both for reading at Ordinary Meetings of the Institution and for publication in the Journal. All Papers, whether for reading or publication, will be submitted to a referee appointed by the Publication Committee.

The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

Pre-Prints.—Advance proofs of Papers to be read at Ordinary Meetings are generally available about a week before the Meeting. Members wishing to be supplied with these pre-prints are requested to notify the Secretary.

Abstracts.—Members and Journal Subscribers desirous of receiving the Abstracts printed on one side of the paper only, can be supplied with these at a charge of 10*s.* per annum per copy, payable in advance.

Issue of Journal.—Members whose subscription is not in arrear receive the Journal free of cost. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address.—Members are requested to notify any change of address to the Secretary.

Benevolent Fund.—The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register.—A register of members requiring appointments is kept at the offices of the Institution, and every effort is made to assist members of the Institution in search of employment.

Members who desire their names and qualifications to be included in this register are requested to apply to the Secretary for the Form of Application for Registration, if they have not already done so. Members residing in the London area are asked, if possible, to return this Form in person and make themselves known, together with their requirements, to the Secretary. It is also requested that members should notify the Secretary immediately they have obtained an appointment.

In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 9.30 a.m. and 5 p.m. daily. (Saturdays, 9.30 a.m. to 12 noon.)

NEW MEMBERS.

The following have been elected or transferred, subject to confirmation in accordance with By-Laws, Sect. IV., paras. 14–15, since the last issue of the Journal:

Members.

Adlington, Reginald Ernest	Abadan.
Hill, J. Bennett	Pennsylvania.
Huch, Victor	Bucarest.
Jacomini, Virgil Victor	New York.
Paterson, Robert Crawford	London.

Transferred to Members.

Evans, Percy	Burma.
Henry, John	Peru.
Reynard, Herbert Corner	Norton-on-Tees.
Samuel, David Leo	London.

Associate Members.

Cock, Jens Nielsen	Oslo.
Halpin, Joseph James Anthony	Dublin.
Kay, John	Burma.
MacDonald, George Anderson	N. Ireland.
McLea, John Hunter	Trinidad.
Muncaster, Thomas Woodthorpe	Abadan.
Perry, Robert George	Trinidad.

Student.

Tiratsoo, Eric Neshan	London.

APPLICATION FORMS FOR ADMISSION.

The Council desire to direct the attention of members who Propose or Second an Application Form for admission to the Institution to the importance of sending a covering letter for the guidance of the Election Committee.

INSTITUTION SCHOLARSHIP AWARD.

On the nomination of the Governing Body of the Imperial College of Science and Technology, the Council have awarded the Institution Scholarship tenable at the Royal School of Mines to Mr. R. O. Young (Student Member). Mr. Young has recently entered upon the first of the final two years of the Oil Technology Course at the Royal School of Mines.

STUDENTS' PRIZES.

Students are reminded that Papers submitted for the Students' Medal and Prize, and for the Students' Prize presented by Mr. T. C. J. Burgess,

must be received at the Institution not later than *30th September*, 1935. Two copies must be forwarded of every Paper submitted.

Full particulars of the Conditions of Award were printed in the February, 1935, *Journal*, or may be obtained from the Secretary of the Institution.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary for insertion under this heading.

Dr. R. L. C. Bleek is home from Austria.

Mr. J. W. Burford has returned from Peru.

Mr. A. E. Day is home from Burma.

Mr. R. W. Farmborough has left Germany and is now in England.

Mr. G. W. Halse has left Venezuela and is now in Trinidad.

Sir Harold Hartley, C.B.E., F.R.S., has been elected as Chairman of the World Power Conference.

Mr. Jack Watson is home from Burma.

Mr. H. Woodfield has left Japan and is now in Australia.

The Secretary would be glad to learn of the addresses of the following members: J. M. Brown, M. Jawad Jafar, J. C. Jones, P. B. M. Linton, A. MacLean, W. J. Reynolds, W. McKechnie Robson, C. A. Sansom, K. A. Spearing, and A. C. Vivian.

ARTHUR W. EASTLAKE.
Honorary Secretary.

CONGRÈS INTERNATIONAL DES MINES, DE LA MÉTALLURGIE & DE LA GÉOLOGIE APPLIQUÉE.

The Seventh International Congress of Mining, Metallurgy and Applied Geology will be held in Paris from 20th to 26th October, 1935. M. Henry Le Chatelier is President of the Congress, and the President of France, M. Lebrun, and Members of the Government have accorded their patronage.

The Congress comprises three Sections, which include the following Subsections having particular reference to petroleum:

Mining Section: Sect. IV. Petroleum:—Drilling; Production; Recovery Methods; Transport and Storage.

Applied Geology Section: Petroleum Geology; Geophysics.

The programme of the Congress includes Works visits and post-Congress tours to various centres. The subscription for individual members is 150 francs for membership of one Section and 50 francs for each additional Section. Full particulars may be obtained from the Secretary, Congrès International des Mines, etc., 13 rue de Bourgoyne, Paris (VII^{e}).

"STANDARD METHODS FOR TESTING PETROLEUM AND ITS PRODUCTS."

The third edition of the Institution's handbook on the methods for testing petroleum and its products has just been published. Since the publication of the second edition in 1929 the Chemical Standardization Committee has been actively engaged in consideration of the existing methods and in the investigation of new methods for specific tests. The results of this work are incorporated in the new edition, which contains nearly 100 pages more than the previous book. Among the new tests are those for Greases (Ash, Consistency, Drop Point, Free Alkali and Acid), Knock-Rating, Existent and Potential Gum in Motor Fuels, Cold Test of Motor Fuels, Dilution of Crankcase Oil, Vapour Pressure, Tests for Liquid Asphaltic Bitumen, and Viscosity in Kinematic Units.

The opportunity has been taken to rearrange the various tests in alphabetical order in preference to classification under products, in order to avoid the large amount of cross referencing under the old system.

A new section has been included for "Tentative" methods, and contains details of tests which are required but regarding which further experience is necessary before they can be considered as "Standard."

Copies of the book, which is bound in cloth, can be obtained from the offices of the Institution, price 7*s*. 6*d*. (To Members of the Institution, 5*s*. 0*d*.) Postage 6*d*. extra.

DEUTSCHE GESELLSCHAFT FÜR MINERALÖFORSCHUNG.

The Deutsche Gesellschaft für Mineralöforschung extends an invitation to the Members of the Institution of Petroleum Technologists to attend its General Meeting in Berlin on the 26th to 28th September, 1935.

The subjects for discussion will include :—

Geology and Geophysics; Prospecting and Drilling; Bituminous Materials; Transport Storage and Distribution; Diesel Fuels; Testing and Nomenclature.

Full particulars of the programme may be obtained from: Professor Dr. Ubbelohde, Deutsche Gesellschaft für Mineralöforschung, Dorotheenstrasse, 40 Berlin.

CONTENTS OF SEPTEMBER JOURNAL.

The following papers are scheduled for inclusion in the September issue of the *Journal*:

"Relationship of Mud to Electrical Coring." H. C. H. THOMAS.

"Thermal Reactions of Hydrocarbon Gases." F. I. L. LAWRENCE.

"Specific Refraction and Other Physical Constants in Connection with the Destruction of Mineral Oils." H. I. WATERMAN, J. J. LEENDERTSE, and G. VAN DE NEWT.

"Alberta Oil and Gas Developments." W. CALDER and R. M. S. OWEN.

VI

Mea
the dim
of the v
many d
dischar
if produ
of flow
intercep
straight
cosity,
increasi
centipoi
defined.
happens
suffices
of "visc

Meas
the allie
have th
obtained
Consisto
thus ind
as the
cylinder
construc
useful fo
paddle r
roughly
figure fo
mobilom
tions of
porting

Appli
and it is
of a mu
received
duction
cuttings

* Preci
Meeting
3 A

VISCOSITY AND THIXOTROPY OF DRILLING MUD.*

By P. Evans and A. Reid (Associate Members).

Meaning of Viscosity. The "viscosity" of drilling mud is dependent on the dimensions of the apparatus used in measurement. The interpretation of the variable viscosity of suspensions has led to much discussion, but for many drilling muds the graph connecting applied pressure with rate of discharge from a long narrow tube approximates to a straight line, which, if produced, cuts the pressure axis at a definite point. For very slow rates of flow the graph is not a straight line, but bends towards the origin. The intercept on the pressure axis gives the *yield-value*, and the slope of the straight-line portion of the graph gives the *mobility*. The *apparent viscosity*, given by the ratio of pressure to discharge, will decrease with increasing rate of flow; consequently the viscosity of a mud stated in centipoises is meaningless unless conditions of measurement are precisely defined. It is better to give figures for yield-value and mobility, but as it happens that yield-value is far more important than mobility, it often suffices to quote the yield-value of a mud, and if a single figure indication of "viscosity" is required, yield-value is the best available.

Measurement. Many viscometers have been used for drilling mud and the allied clay slips of the ceramic industry. Simple efflux viscometers have the drawback that, unless used in groups, only a single reading is obtained, and this may have little direct relation to yield-value or mobility. Consistometers will give a series of points on the flow–pressure graph, and thus indicate both yield-value and mobility. A viscometer with air pressure as the driving force gives a greater range of readings. The concentric cylinder instruments, except in their simplest forms, are complicated to construct and use. A very simple form of paddle viscometer has proved useful for drilling mud and cement slurries; the force required to start a paddle rotating in the mud is measured; this is, for any one type of mud, roughly proportional to the yield-value. The shearometer gives a rough figure for yield-value, but accurate work presents certain difficulties. The mobilometer is also useful for thick muds and cement slurries. Determinations of the yield-value from the maximum torque possible in a wire supporting a cylinder immersed in the mud involve some complications.

Applications. The importance of viscosity has long been recognized, and it is often thought of as the most typical distinguishing characteristic of a mud, but detailed applications of viscosity figures have hitherto received little attention. Viscosity measurements should aid in the production of mud requiring minimum pump-pressure consistent with carrying cuttings, mudding-off sands, and building and maintaining a good wall.

* Precis of Paper presented for discussion at the One Hundred and Sixty-fifth Meeting of the Institution of Petroleum Technologists, May 14, 1935.

Investigations are needed to determine (*a*) the laws of flow in the circulating system, and (*b*) the factors which alter the viscosity of mud.

When rotary mud is forced through a narrow pipe, it first moves forward very slowly as a plug; with greater pressures the outermost layers shear into telescoping cylinders, a central plug remaining; this becomes smaller, until eventually all the mud moves forward in telescoping cylinders in a manner similar to viscous (stream-line) flow; with still greater pressures flow becomes turbulent. The lower critical pressure at which the mud begins to shear is theoretically three-quarters of the yield-value pressure, but in practice is usually less. The higher critical pressure at which "plastic" flow changes to turbulent (or hydraulic) flow is, it seems, roughly determinable by taking the "apparent viscosity" of the mud in place of the viscosity of Reynolds' equation, and turbulent flow in wide pipes may commence at a pressure very near the yield-value pressure before dominantly plug flow can pass into dominantly stream-line flow. Despite the difficulties in utilizing results of capillary tube measurements for predicting the flow of mud in circulation, it seems likely that approximate flow-pressure diagrams will be obtainable from an application of principles deduced from these measurements. Flow in the circulating system is probably near the stage at which the mud changes from plastic to turbulent flow; with slow circulation the flow will be plastic, but with normal or rapid circulation it is likely, for average mud, to be turbulent in the drill-pipe but possibly not throughout the annular space.

Changes in Viscosity. Viscosity varies with differences in composition and history. Weight and yield-value are related by an approximately exponential law. Suspensions with finer particles are more viscous, and maturing and agitation bring about changes in yield-value and, to a smaller extent, in mobility. Temperature has an important effect on yield-value, and many muds undergo partially reversible changes when heated.

Thixotropy. Some muds, especially those that have received extensive chemical treatment, will gradually set to a jelly-like mass, but will return to a mobile liquid if agitated, and again set to a jelly if allowed to remain undisturbed. A smaller degree of thixotropy shown by many muds consists of a gradual increase in viscosity when the mud remains undisturbed and a rapid decrease when the mud is agitated. This greatly complicates viscosity measurements. There has been confusion between variable viscosity of plastic flow and the change in viscosity produced when a thixotropic substance is agitated, and also between thixotropy and yield-value.

The thixotropy of markedly thixotropic muds can be measured by filling a number of test tubes and finding the interval elapsing before a tube can be inverted without spilling its contents. Viscometric methods of measuring thixotropy involve the difficulty that, although the mud should remain undisturbed, the measurement necessitates some degree of disturbance, but approximate evaluations can be made by neglecting changes in mobility and estimating yield-value at intervals by the paddle viscometer or shearometer.

Thixotropy in a mud has both advantages and disadvantages. A thixotropic mud combines some of the properties associated with high and low yield-values, and since there are times when each of these is valuable,

the combination may be very useful, but very thixotropic muds have disadvantages, *e.g.* when long strings of casing are being run. Some of the effects of thixotropy in the well are merely those of a much-enhanced yield-value, but in the flow relationships new phenomena appear. The yield-value will be less at the circumference of the mud stream, where the rate of shear is greatest, and flow will tend to consist of a plug or core of relatively undisturbed viscous mud separated from the drill-pipe by a zone of highly sheared mobile mud. Following Mr. W. E. V. Abraham, this type of flow may be termed "lubricated flow," and it presumably follows laws differing from those of plastic, viscous, and turbulent flow. Lubricated flow is likely to pass directly into turbulent flow as velocity increases.

The difficulty in predicting flow–pressure relationships for the circulating system of a well, especially with thixotropic mud, indicates the need for detailed investigations aiming at the correlation of well and laboratory data, the work hitherto done not being commensurate with the importance of the subject. Even the actual cost of drilling mud, quite apart from the large sums of money invested in drilling in difficult territory, and the increased risk of total loss if the mud is unsuitable, demands a much more extensive study of the subject than has as yet been undertaken, and the resulting better understanding of drilling-fluid is likely to have a very great money-saving value.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Sixty-Fifth General Meeting of the Institution of Petroleum Technologists was held in the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, May 14th, 1935, **Mr. Ashley Carter** (Vice-President) in the Chair.

The following paper was presented:

VISCOSITY AND THIXOTROPY OF DRILLING MUD.*

By P. EVANS and A. REID (Associate Members).

DISCUSSION.

Professor V. C. Illing said there were one or two points on which he would like general information. For instance, he would like to know what amount of temperature control had been adopted by the authors in their work. In the speaker's experience careful temperature control was essential in such work, and some of the experiments described appeared to lack this precaution.

One small point of issue which he had with the authors was with regard to the matter of measurement of viscosity in capillaries. In Hobson's work the author seemed to consider that a small capillary was a difficulty. As a matter of fact, Hobson had worked with various sizes of capillaries, and if accurate results were desired one must have a certain limiting capillary diameter unless the apparatus became cumbersome in length. He agreed with the authors that a mere statement of viscosity in terms of so many centipoises was meaningless in the case of muds unless one gave a complete series of values and the conditions of the experiment.

He would like to know more fully how far the results of the paddle viscometer were reproducible in different instruments.

With regard to the rotating cylinder viscometer, he did not know whether the authors had met with the same difficulty as the speaker and his colleagues, that as soon as one started rotating many of these fluids sedimentation was accelerated; and the types of mud became rapidly differentiated.

Another point he would like to raise with Mr. Evans was as to his experience with the shearometer. Mr. Evans had not said very much about it. The speaker and his colleagues had worked with the vane type of shearometer, and he was afraid they had got no reproducible results which were of any value. He did agree, however, that some sort of shearometer based on a rotating cylinder immersed in the fluid, or one such as Mr. Evans had mentioned that evening, did give very interesting results.

There was one other point with regard to plug flow. Mr. Evans had

* See pp. 677–679.

mentioned a water film. In the work done at Rothamsted they were very careful to mention that there was a fluid film at the edge; but they had never used the term "water." As a matter of fact, there were certain physical conditions in a mud where one could induce, and did induce, a water film; but in his own experience it was only by very special methods of filling. He would like to know on what evidence Mr. Evans claimed the presence of the water film, and what special methods he had used in filling his apparatus, or alternatively what were the conditions which he found governed the occurrence of the water film between the mud and the viscometer.

With regard to Mr. Evans's last remarks, he would like to support the need for more big-scale experimental work. There was an immense amount of money being spent on muds, and he personally felt that the earlier the Companies got to considering that a well was a large-scale viscometer, and treated it as a viscometer, and got all the values out and then compared them with laboratory results, the sooner they would get to a more complete knowledge of the laws governing mud flow in drilling wells. At the present moment too little was known about the forms of flow which were occurring within the drill-pipe and the annulus between the drill-pipe and the casing. The whole problem was so difficult that it was only by careful laboratory work co-ordinated with large-scale practice that any real progress would be made.

Professor H. Freundlich said the authors had dealt with many things, some of which he had known already and some of which he had often tried to figure out in his imagination. He had been most pleased to find that all sorts of things which he had done in the laboratory had proved valuable for practical purposes.

Since the members had heard about the phenomenon of thixotropy, they might be interested to see the actual phenomenon. He had brought with him a few samples, one of which had the property which Mr. Evans had mentioned, namely, that it could be heard but not seen.

The first specimen was that of an aluminium oxide gel. On being shaken it became fluid, and after a few minutes it became solid again.

The second sample was that of an iron oxide jelly. Those present would see, again, how it became quite liquid when shaken and returned to solidity after a few minutes.

The next sample was one which could not be seen, but only heard or felt. That was a mud made from a special slate in Germany with a certain amount of water. It became solid in an instant after shaking.

Mr. Emil Hatschek said he knew what it meant to study in the laboratory a single colloid which had the unfortunate property of altering with age; but when it came to substances which not only changed with age, but also with rate of shear and various other factors, then the task was one which was enough to appal the stoutest of hearts.

Personally, he had never worked on muds, and he had not been a profound believer in the yield-value. Prof. Freundlich and himself had never found anything which could be called a "yield-value" in colloidal solutions. He was compelled, however, on the evidence put before him that evening,

to accept that there was such a thing, and that it was an important technical constant and, in fact, it seemed to be technically more important than viscosity. If one had to set a mass of anything moving, the effort in starting was the factor which would determine one's machinery; whereas what it did afterwards was comparatively unimportant, as long as the effect was less than what it had been at the beginning. That made the technical importance of the yield-value extremely interesting. When it came to thixotropy, that was where the real trouble began. If one wanted to study thixotropy theoretically, and if one then wanted to deduce technical applications from it, it seemed to him that one had a difficult task. In the formula which was pretty generally accepted now as representing variable viscosity there were three constants. The physical meanings ascribed to those constants were that of viscosity at a very low rate of shear, viscosity at a very high rate of shear, and a thing which authors called "modulus of elasticity." It did not matter what they were called as long as they had the proper dimensions.

Coming to thixotropic substances, one obviously could not be satisfied with three parameters. He was assuming that one could measure the viscosity of a thixotropic system at any given moment; this could be done at least as a "mental experiment," but he did not see how it was going to be done practically. Assuming, however, that it could be done, one would then get a family of curves each of which could be represented by three parameters, and the whole family with one further parameter—which was time. What could one do in that way? First of all, even if one could overcome the initial difficulty of measuring the viscosity of the thixotropic system at any one moment, what one was going to do with the data did not seem to be clear or hopeful. What brought about increase in viscosity was at present a complete mystery. Yet an idea had to be obtained of what brought about that change before a practicable method of measuring the change could even be thought of. He did not know whether all this arose in practice. Personally, he thought, in technical work, one had to deal with extremes. He did not know that any thixotropic theory was going to make any difference.

He had been interested in the flow diagrams, because the type of flow in the colloidal solutions with which he was more familiar had been the subject of a great deal of debate and a great deal of *a priori* prophecy and conjecture, until it had been actually investigated by Kroeppelin in the Hydrodynamic Institute in Goettingen by proper methods when, instead of the usual parabola, he found a flat parabola. Before that—and even now—the question of whether one could get laminar flow at all in a system of this kind had been an open one.

Personally he had been surprised to hear that most of the flow with mud was turbulent flow. It had, of course, to be remembered that turbulent flow could set in in colloidal solutions at lower rates of shear than would be expected from their apparent viscosity. As a matter of fact, he thought that he and his collaborator, R. S. Jane, had been the first to demonstrate this anomaly for ammonium oleate solutions, which were liquids of comparatively low variable viscosity, but exhibited turbulent flow at lower rates of shear than pure water.

At the same time, he could not help being struck by the existence of

turbulent flow in systems like muds, which had high yield-values and high viscosities. As for representing the results, he was afraid there was nothing for it except to express them by an equation involving at least three constants. One would never get a single figure representing a property which varied both with the rate of shear and with age. That was where investigation was desirable, and he must leave it to the technical men—and wished them every success in their efforts.

Mr. A. de Waele congratulated the author of the paper on having taken his audience, in the space of about an hour, from the commencement of the first principles of viscosity in liquids to the equally difficult conception of thixotropy. He desired also to congratulate him on having sifted out in so many words the distinction between thixotropy as a temporary change in the constants of so-called fluidity and yield-value with disturbance and subsequent rest, from the phenomenon to which the term thixotropy had often been applied, viz. the variability of these same factors with the rate of shear. The two things were entirely different—that was to say, most heterogeneous substances showed a variation of so-called viscosity or consistence with the rate of shear, whereas the phenomenon of true thixotropy was shown by a certain restricted number of substances only.

One matter on which he would like information was, did Mr. Evans find thixotropy to be necessarily confined to any particular types of muds—*i.e.* was it shown by an artificial "mud" in which the disperse phase was as spherical as *e.g.* the particles of carbon black? He had in his own experience failed to discover thixotropy in such a system. He had, on the other hand, found that substances with an acicular disperse phase which was capable of orientation under certain conditions did show it very markedly. For instance, bentonite sludge showed thixotropy strongly when shaken in a tube. Personally, he had no very great experience of muds, but a markedly thixotropic substance was to be found in petroleum jelly. This material showed certain phenomena of thixotropy which he had been entirely unable to explain. He would like to quote his experience with it in the hope that Mr. Evans might supply an answer. If one sheared petroleum jelly through a number of capillaries having the same radius but different lengths, one could thereby obtain the same rates of shear by varying the shearing stresses. The time, however, during which the material was subjected to a given rate of shear would be proportional to the length of the capillary—in other words, the ratio L/R. In those circumstances a lowered intercept ("yield-value") and a raised mobility were obtained as the length of the capillary was increased; or, in other words, with the period of time during which it had been under shear.

The deflocculating effect of capillary shear could also be matched by grinding petroleum jelly in a pestle and mortar. The thixotropic effect of lowered consistency—which was a combination of lowered "yield-value" and raised mobility, persisted for quite a time—several days.

If another type of apparatus was used to disturb the structure of petroleum jelly, viz. a granite roller mill—(or, alternatively, another little apparatus familiar to housewives, a cream-maker, which was to all intents and

purposes a viscometer in which definite turbulence was induced by passage through a narrow and a wide capillary alternately)—the reverse effect ensued; one got an increased consistency. He had a difficulty in understanding the explanation of those phenomena. Could it be that with one type of disturbance, the acicular crystals of petroleum jelly were oriented in a direction parallel to the rate of flow (by stream-line flow), and that in the case of the granite roller mill grinding, or cream-mixer "capillary" shear, in which pure tangential shear was impossible of conception, random deorienting of the crystals would occur with resulting rise of consistence?

Mr. Scott Blair confessed that he was the culprit who had introduced the words which Professor Illing had mentioned, namely, "water layer." If he might say one word about that, he had wanted to be vague. He had known that a paste of mud was going through a tube, and he knew that he did not get solid friction between a dry surface of mud particles against a dry surface of glass. Something was in between. That something was H_2O, and that H_2O was not ordinary fluid water. That was why he had used the term.

With regard to the question of the yield-value coming out low in the rotation instrument, he wondered if that was because Mr. Evans was not really measuring the yield-value there at all, but was measuring "A"? If one rotated cylinders of metal in mud pastes the result which one obtained corresponded far more closely to the "A" on Mr. Evans's diagram—(that was to the point at which the plug started to flow)—than it did to the real yield-value itself.

He had to confess that when he had heard all this business about turbulent flow so near the yield-value he had felt that it could not be real, although he had actually seen the graph. When one began to think about working out critical numbers, and things of that sort, and using for one's viscosity in the equation the ratio total shearing stress/rate of flow, it did appear to him that it was a terribly complicated business altogether, and one which was not yet at all understood.

As to the specific nature of thixotropy, he did not know if it was generally known that honey derived from one single plant, *Calluna vulgaris*, was highly thixotropic, but in the case of something like twenty-five other honeys which had been examined, even from the similar species of *Erica cinerea* and *Erica tetralix*, there appeared to be no signs of thixotropy.

Mr. Hatschek had mentioned the three constants. Personally, he thought perhaps the reason why the third constant had always tended to be neglected in the case of materials like muds—why those interested had tended to work on the two viscosities alone—was because the rigidity modulus was really so high compared with the viscosity. For example, ordinary flour dough had a viscosity of the order of 10^6, and a rigidity modulus of about 10^4. With mud pastes, the modulus corresponding to such a viscosity must be enormously high. In systems of that kind one could, from a purely "practical convenience" point of view, talk about the two constants, one being viscosity at high stresses and the other at low stresses. Again, for convenience, it was very often profitable to take some kind of rough measure of elastic limit instead of the latter viscosity.

His last point was another confirmation of the importance of yield-value as distinguished from viscosity. His own particular interest was in farming, and at Rothamsted they had been measuring some of those properties for soils. If one took pieces of soil from different parts of a field and made those soils up into pastes, one got a very high correlation between the yield-values of the pastes and the pull required to draw the plough through the particular place from which the soil had been taken; whereas if one tried to correlate the mobilities with the pull on the plough, the correlation was nothing like so good. The things which seemed to be correlated with mobilities were very much more factors that could be induced, for example, by artificial chemical treatment; but the shear resistance—or the work that had to be done—was very much better correlated with some rough measure of elastic limit.

Dr. A. B. Manning remarked that he had had no experience with muds, but he had been led to a study of a similar type of system by some recent work which had been carried out at the Fuel Research Station on suspensions of pulverized coal in oil. Such suspensions appeared to possess many of the mechanical properties which had been described that evening by Mr. Evans, and his own examination of the literature on such systems had shown that there was a very great need for a further study of the type of system which lay between the purely colloidal system and the coarse suspensions. There seemed to be very little accurate knowledge existing about such systems.

One point had struck him—namely, that if a viscometer could be used of a type in which the material was subjected as nearly as possible to a pure shear, the information should be of a more fundamental character perhaps than that obtained by the capillary tube type of viscometer. In the capillary tube there was that big variation in the rate of shear, from zero at the centre to a maximum at the circumference of the tube. He thought that might tend to complicate the results—or at least to render them less easy to analyse. Personally, he would suggest that the rotating cylinder type of viscometer would be more useful in studying the fundamental properties of such systems than the capillary tube type, for the reason that one could get nearer to a true shear. It might be possible to get closer still by designing an instrument with that point of view in mind. He realized that such an instrument would possibly be of a certain complexity and difficult to manipulate, and that that might take it out of the field of practical politics in an examination, say, in the field of this type of material.

Dr. G. Barr said that he would like to mention a point which did not appear to have been raised before regarding the interpretation of flow-pressure diagrams of the Bingham type. The authors showed that when mud was forced through a tube of internal radius r_1 there was a stage during which the flow consisted in the translation of a central solid plug, of radius r_0 decreasing with the rate of discharge, while laminar flow occurred between r_0 and r_1. If the material had a relatively high yield-value, it did not appear improbable that turbulence should occur in the annulus before the plug radius r_0 became vanishingly small. Persistence

of the plug would be favoured by the fact that the rate of shear at its surface would be reduced when the laminar flow broke down.

Similarly, it must be assumed that between the outside of the drill, of radius r_2, and the wall of the casing, of radius r_5, there would exist under suitable conditions an annular cylinder of solid mud having internal radius r_3 and external radius r_4: at low rates of discharge laminar flow would occur between r_2 and r_3 and between r_4 and r_5. The rate of shear being higher at r_3 than at r_4, it was possible that turbulence might develop between r_2 and r_3 while stream-line conditions persisted between r_4 and r_5. In dealing with muds of high mobility and high yield-value, this possibility would complicate the diagram relating rate of discharge to pressure.

Dr. A. E. Dunstan remarked that those present had listened to an extraordinarily interesting paper and discussion, but admittedly they were left very much where they had been from the point of view of the theoretical implication of the subject. At the same time, however, the fact that the attention of physical chemists had been directed to the phenomena which were taking place in the flow of these viscous and plastic systems was all to the good, and there was no doubt at all but that work on these lines would lead to practical results.

Mr. A. F. Dabell thought that the discussion should not be concluded without the view-point of the driller being expressed.

Speaking with full appreciation of the value of better understanding of the properties of drilling mud, after listening to the scientists discussing the question, it occurred to him that unless acceleration was applied to their studies, it might be found that mud would no longer be required in oil-fields before their decisions were arrived at.

One suggestion he advanced was that mud had no thixotropic properties which, with the authors' permission, he would refer to as gelling.

He had never seen a mud composed of clay and water gel. Drilling mud sometimes did so in even quicker time than the 80 seconds to which reference had been made; but it applied, so far as his own observations went, only to muds to which some foreign matter had been added.

In drilling an oil well to-day the most serious problem arose from the gassing of mud, which was costing much money, and even at times was responsible for loss of life.

It occurred occasionally when the drilling tools were being withdrawn from a well through thick liquid. The gas in following the path of those tools gradually reduced the density of the mud, until the content of the well went up into the air, the gas following before due preparation for its control could be made.

It was an easy matter to mix barytes, clay and water in regulated amounts to give an ideal mud, but to prevent the change of nature of that mud during the process of drilling did not seem possible.

The chemist could sample the mud from a well and return from the laboratory in ten minutes with suggestions to overcome a difficulty, but if in the meantime there has been a tropical rainstorm, or the driller has drilled one foot into an entirely different substance, the mud was then entirely different in its nature, and the suggestions valueless.

What was really wanted was a liquid through which gas could bubble out, as it did through water—a mud with low viscosity and low rate of gelation.

Unfortunately, however, low viscosity meant greater penetration. In fact, the thinnest mud was used to kill high-pressure gas sands.

When drilling into an oil sand it was essential that the mud be of such nature that a cake of clay be formed by filtration upon the face of the sand as drilling proceeded, and that the quantity of filtrate be infinitesimal.

This filter-cake, moreover, must not exceed half an inch in thickness, otherwise there may be additional penetration after each insertion and withdrawal of the drilling tools. Incidentally, experience has shown that an insignificant back pressure would remove this cake from the face of the sand, and that oil was its solvent.

The drillers' practice to reduce gas cutting of mud was to drill as slowly as possible into and through the sands containing gas, at the same time circulating as great a quantity of mud as possible in order to reduce the percentage of gas in every cubic foot of mud.

Their practice to reduce viscosity was to add soda to the drilling mud. On the other hand, if the driller wanted to increase the viscosity, cement was added.

Mr. Evans had referred to gelling as a disadvantage in running a long string of casing.

In running a long string of casing, his own opinion was that gelling really was an advantage, inasmuch as it prevented the settling of cuttings in the interval between the withdrawal of the tools from a well and the running of the casing—sometimes a matter of nine or ten hours.

In general, good drilling called for mud of minimum viscosity to give release to gas and maximum weight to hold pressure in control, and he asked the authors what were the features dominating attainment of this end.

He added that for purpose of comparison of viscosity in Trinidad a measure, evolved by Mr. Richard of the Apex Company, was in use among the drillers which was based upon the time of efflux of 750 c.c. of mud through an orifice $\frac{7}{32}$ of an inch in diameter and 3 inches in length.

Mr. P. Evans, in reply, said Professor Illing had referred to the question of temperature control. In Assam they had tried to get over the difficulty by using a large quantity of mud and getting the experiments done quickly before the temperature changed; from one experiment to another the temperature might be slightly different, but if there was a series of experiments over a considerable range of temperature, it was possible to apply corrections, and this seemed to be near enough for much practical work.

With regard to the size of the capillary, that seemed to be a matter where Professor Illing and himself must agree to differ. His colleagues had found that the large ones worked very well and seemed to avoid trouble from that curved part of the graph which was very interesting theoretically but was rather a nuisance in practice. The Rothamsted work was done with moderately large capillaries.

Mr. Evans thought that paddle viscometer results were reproducible,

but different instruments needed calibration against a standard instrument; possibly the best way to make use of the results was to employ some other type of viscometer for standardization purposes and to convert the readings from the paddle viscometer into yield-value in dynes per square centimetre.

With reference to shearometers, he had not altogether given up experiments on shearometers, but his colleagues had encountered the difficulties which Professor Illing had found, namely, that the shearometer after dropping to a certain distance and then becoming almost stationary would drop again, and possibly even again. In some cases it seemed to be due to a film of water actually separating on the surface of the shearometer.

As to the question about the water film in a capillary tube, he admitted that he ought really to have used the term " fluid " in that particular case, but as there had not seemed to be any other fluid available he had thought that perhaps " water " would convey the meaning just as well as anything else, and he felt that Mr. Scott Blair had already accepted the responsibility.

He particularly welcomed Professor Illing's emphasis on the need for large-scale work.

He did not think there was anything to refer to in Dr. Freundlich's remarks, except to thank him for demonstrating so very clearly what he himself had asked people to take on trust.

He agreed with what Mr. Hatschek had said—that it must not be supposed that yield-value was in any way a universal property. Nevertheless, it did seem a very useful conception where drilling muds were concerned—and his remarks had been confined entirely to those particular substances. In mud problems so much money was at stake that technologists must do their best to get some sort of guidance whatever the difficulties were, and it was probably as well to work, as Mr. Hatschek had suggested, with extreme instances.

A point of view which was rather new to him had been indicated by several speakers, who had expressed some degree of surprise at the occurrence of turbulent flow in the circulating system. It had been very generally accepted in such little literature as there was on the subject that the flow in the circulating system of a rotary well was almost entirely turbulent, and he had been trying to see whether that was really the case and had felt rather diffident in suggesting that the flow might not always be turbulent. It was refreshing to have the problem approached from an entirely different angle and to hear people saying that it seemed rather surprising that it was turbulent.

Mr. de Waele had asked if thixotropy was confined to any particular type of mud. Mr. Evans's experience was that it was found most strongly developed in muds which had been chemically treated, but that most muds seemed to show thixotropy, if only slightly.

The behaviour of petroleum jelly was most interesting, but he was certainly not competent to venture on suggestions as to possible explanations.

Mr. Scott Blair suggested that perhaps in some cases he and his colleagues had been measuring the point " A " on the flow–pressure curve. That was a thing which they had themselves suspected, and he had been rather hopeful that before now they might have been able to settle the point, but

work of this type had to go on intermittently as opportunity occurred, and they had not got very far in elucidating the relationship between what might be tentatively termed the shear force and the true yield-value. So far the experiments seemed to suggest that, with the shearometer, they were rather further along the curve than the point "A"; that was, that they were somewhere in the neighbourhood of three-fourths of the yield-value, but it was a matter which was still very far from being settled.

Dr. Manning had emphasized the desirability of getting a pure shear and avoiding the complication of the variable shear in a capillary tube. Mr. Evans agreed with that, but unfortunately with substances like drilling mud the rotation viscometer was an awkward instrument to work with; he thought for certain research purposes the concentric cylinder viscometer should be employed, although it was hardly the kind of thing that could be used in the oil-field laboratory for routine work.

Dr. Barr had referred to the flow in the annular space and had pointed out some of the difficulties. There were so many of those that he was afraid that he and his colleagues had not yet gone very far with the problem of what was happening in the annulus. It was a matter which called for a good deal of further inquiry.

Mr. Dabell in his remarks had gone rather further afield than the actual scope of the portion of the paper read that evening. He had said that he had not seen a mud which was really so thixotropic as to set to a gel. That remark had filled him (Mr. Evans) with astonishment until he had realized that Mr. Dabell had been speaking of something entirely different from what he himself had been speaking of when he had been using the term "mud." Personally, he did not restrict the use of the term "drilling mud" to the simple clay–water mixture and could see no reason to do so. He agreed that he had not seen a thin mud containing nothing but an ordinary clay and water which would, on its own, set to a gel, but if a bentonitic clay was mixed with water, one then had something which would set very easily to a gel, and most of the heavily "treated" muds would set to some sort of gel, even if it was not a very firm one.

The question of gas-cutting was of great importance. That was associated, he thought, more particularly with the yield-value, and in attempting to reduce the yield-value to a minimum they were getting the most favourable conditions for eliminating trouble with gas.

He might mention in connection with this question of gas-cutting the advantage of being able to put the well under pressure at very short notice and the very great ease with which a well equipped for pressure drilling could be controlled, particularly when the drill-pipe was being withdrawn.

Mud problems usually needed very careful co-operation between the geologist, the chemist and the driller. That was a point which could not be too much stressed. If the chemist confined his work to the laboratory and never went on to the well, not very much progress would be made. The geologist must also be concerned in the matter; he might have to supply the clay, and he would certainly have to predict the depth at which various formations which were likely to give trouble might be expected.

The formation of the filter-cake depended very largely on viscosity and on the type of mud; but he was afraid that to discuss that now would take him rather too far afield.

A point which evidently was not quite clear in the precis was the possible disadvantage of very thixotropic muds when casing was being run. It might be that a day or more was occupied in running the casing to a depth of 8000 or 9000 ft., and during that time the mud might take such a firm set that it was quite impossible to break circulation when the string had reached bottom. There were several recorded instances of deep wells in which a string of casing had been lost simply because the mud had been extremely thixotropic and had developed such a high yield-value during the time the casing was being run that when an attempt was made to start up the pumps, circulation could not be obtained and the string could not be cemented.* A small degree of thixotropy was an advantage in most circumstances connected with the drilling of wells.

In amplification of his remarks, Mr. Evans writes further :—

A number of points raised in the discussion, particularly several mentioned by Mr. Dabell, are referred to in more detail in the full paper than was possible in the precis or in the meeting. Mr. Dabell's plea for greater acceleration in mud investigations is entirely in accord with the comments of Professor Illing, and is, indeed, one of the main theses of the paper. It is, however, difficult to follow Mr. Dabell in his description of the effects of a tropical rainstorm, or of drilling one foot into different strata. Much of the authors' experience has been gained in the wettest country in the world, and the effect of a heavy storm on the mud in circulation is very small unless pits and flumes are so ill-constructed as to catch ground drainage. In important wells, where drilling is difficult, the mud circulation system is entirely covered over by rough shelters—often of junk corrugated sheeting. If the arrangements are so defective that ten minutes' rain can entirely change the properties of several hundred barrels of mud, most of which is actually in the well itself, the fault lies not with the chemist, but with those responsible for the lay-out of the well. Similarly, the contents of a foot of new strata can affect only a limited volume of mud in only a very limited number of ways; if this emergency could not be dealt with at once by the chemist responsible for advice about mud, then there would seem to be a clear case for acquiring a new chemist, it being assumed, of course, that the well was adequately equipped in advance with efficient arrangements for mixing and storing mud, and that the chemist was not entirely new to his job.

The Chairman, in proposing a very hearty vote of thanks to the authors for their exceedingly valuable paper, said that he was sure those present would wish also to express their gratitude to the Burmah Oil Company for allowing the authors to give the results of their exhaustive experiments in connection with the important subject of drilling mud.

The vote of thanks was carried by acclamation.

* Parsons, in a paper at the 1934 Tulsa meeting of the Petroleum Division of the A.I.M.E., records three instances in wells over 9000 ft. deep in which the casing was lost through excessively thixotropic mud, and estimates the direct cost of casing alone at £20,000 and the total investment at stake as £100,000.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

RUMANIAN BRANCH.

A GENERAL MEETING of the Rumanian Branch of the Institution of Petroleum Technologists was held on November 2nd, 1934, when the following paper was presented :—

THE DEVELOPMENT OF WIRE ROPE PUMPING IN RUMANIA.

By PERCY R. CLARK (Member) and LUTZ F. W. SCHROPP.

Some of the undoubted advantages and particularities of wire rope pumping are :—

1. Greater speed in lowering and extracting the plunger. As there are no couplings to unscrew, this means a very considerable economy in time and labour. The objection can be raised that a normally working pump may go six to eight months before it is necessary to pull it out, and a few extra hours spent in withdrawing and replacing the piston are not of much account. However, that is not entirely the case, as production is likely to be more steady if the plunger is subjected to constant supervision. With a wire rope this takes only 15 to 30 minutes, and one can thus inspect the plunger, repair the liner, and generally clean out the valves, etc., every few days.

This constant extraction of the plunger is more particularly important in the case of wells containing paraffinous oil. To avoid tubing becoming choked up, the pump has to be extracted almost daily. In such circumstances rod pumping may not be a paying proposition. With rope pumping, however, by attaching a paraffin cutter to the rope when extracting the piston, the tubing can be easily cleaned out and an accumulation of paraffin sediment avoided.

2. With the wire rope cheaper pumps can be used than is the case with rod pumping.

A pump used by one company consists of a hard, polished, long steel cylinder without any liners. Below there is an ordinary foot-valve and gas anchor. The piston consists of separate rings of soft bronze, which reduce the wear on the steel cylinder, but, on the other hand, the rings are in themselves strong enough to withstand four to six weeks' pumping. These pistons were manufactured in the company's own workshop, and proved very resistant to wear by sand, and much cheaper than those of chrome leather, composition cups, etc. The plunger is made up of about ten to fifteen soft bronze rings of 3 cm. width each, and they are put on a guide tube, with upper and foot-valves.

Furthermore, if the foot-valve is constructed on the dismountable principle (Ritterventile) it need never be taken out.

3. The connection between the plunger and the rope is made by means of a rope socket attached to a sinker bar.

The disadvantages of a rope, as compared with sucker rods, are its flexibility and stretch or elongation tendency and, in certain respects,

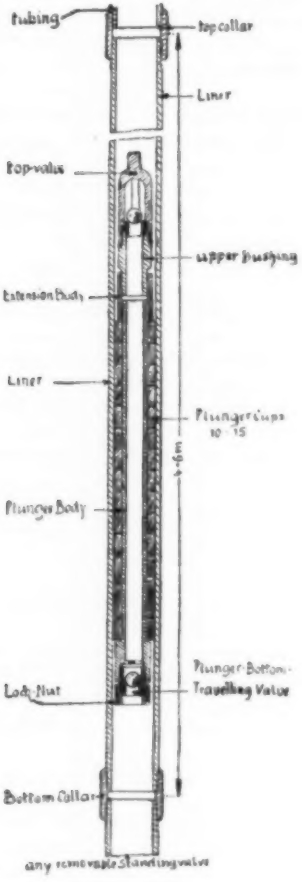


FIG. 1.
PUMP.

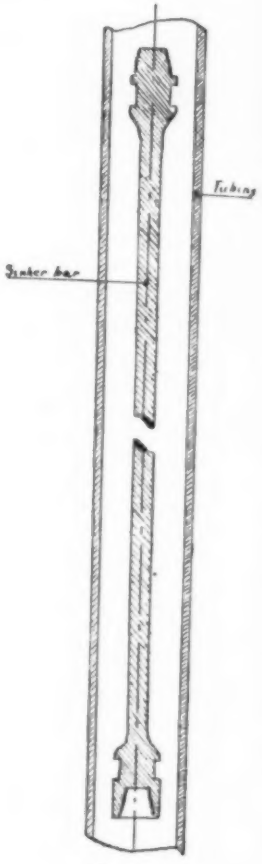


FIG. 2.
SINKER BAR.

its elasticity; therefore the effect of these inherent qualities of the rope must be modified.

To this end the rope is weighted by means of sinker bars attached to the lower end, the amount of this weight depending on the depth of the well and the size of the pump. The movement of the pump must be carefully watched in order to ascertain exactly the right number of sinker

bars to be used, and for this purpose a few bars only are first placed in position, and then gradually added to until the pump is working quietly, without shock, and giving a regular flow of liquid.

At the commencement, in order to ascertain more exactly the weight required, tests can be carried out by means of ordinary sucker rods. This is especially important when a new rope is placed in work, as particular care should be taken to avoid overstretching a rope before it is set.

In view of the inherent tendency of the wire rope to elongate at the commencement of work, it should be inspected every hour during the first twenty-four, and after that, say, once a week, in order that any elongation that has accrued may be taken up. Excessive elongation of the rope can be recognized by the shortening of the pump stroke, which must obviously take place as the piston sinks deeper. Sometimes the stretch is detected by the vibration arising from the knocking of the piston against the foot valve.

When a pump fitted up as indicated above is in use, the elongation of the rope plays a less significant rôle. In such pumps the ratio of the stroke to the length of the cylinder is small, and more room is thus left, while the rope is elongating, for the normal working of the plunger to continue.

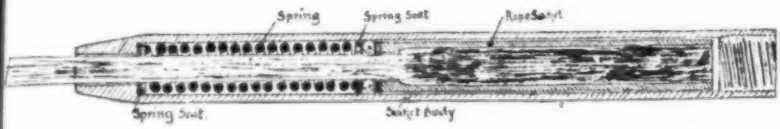


FIG. 3.

ROPE SOCKET.

4. As regards the rope itself, the greatest attention must be given to the two extremities, viz. the point where it is attached to the rods and pump, and the part where it is attached to the balancing beam or chain drive. Experience has shown that these are the parts where the rope wears out most quickly. Unfortunately, the part of the rope near the plunger is not as a rule frequently inspected, and consequently most rope breakages take place there.

It will be found, furthermore, that these breakages generally occur when the weight ratios have not been correctly established, *i.e.* when, owing to friction on the cylinder, the speed of the downward stroke of the piston is less than that of the rope. In this case, kinks are formed in the rope immediately above the sinker bars, and the protruding part is quickly worn out against the casing walls.

There may also be a defect in the construction of the rope, *e.g.* a twist tendency left in which causes rotation of the rope in the well. This twist tendency is not removed by the stress engendered during work, but can be counteracted to a certain extent by a specially constructed rope socket. For this purpose, a swivel rope socket with ball bearings and shock absorbing springs is recommended. The ball bearings ensure the torsionary adjustment of the rope by free rotation, and the springs lessen the shock arising from the upward movement of the plunger.

The main point is, as with all Canadian pumps, that the stroke should be as long as possible, and the number of strokes per minute as few as possible. By this means, not only the rope but all the other parts of the outfit—*e.g.* pump valve springs, ball bearings, etc.—are preserved.

The upper end of the rope, *i.e.* the part near the connection between the rope and the balancing beam or chain attachment, is easier to control. Difficulties here arise at three points:

a. At the stuffing-box. As the *raison d'être* for the stuffing-box is to stop the passage of gas and oil alongside the rope, the packing should theoretically be 100 per cent. tight.

With pump rods this degree of perfection is perhaps attainable by the insertion at this point of a polished rod, but in the case of a wire rope, with its unavoidably uneven surface, the possibility of using either hard

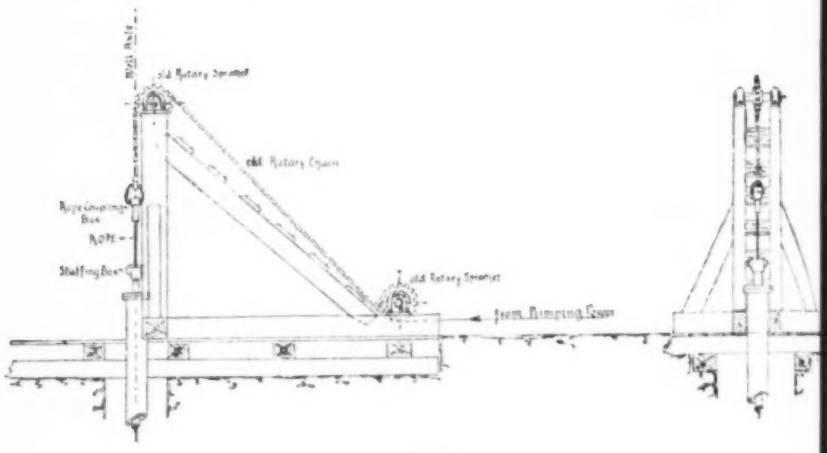


FIG. 4.
CHAIN ATTACHMENT.

metal packing or soft leather or hemp packing is excluded, owing to the inevitably rapid wear that would ensue.

There is the possibility of obtaining a tighter packing with rubber, or perhaps better still with loose metallic packing which can be made to fit into cavities of any shape.

b. Accurate centring of the rope. The best stuffing-boxes and packings are of no use if the rope is not properly centred.

It has been proved that it is better to use the chain attachment rather than the ordinary balancing beam which is so much in vogue in Rumania.

On an ordinary wooden or iron frame is fitted a rotary chain wheel seated in a plummer block, and so placed that the longitudinal axis of the bore-hole is at a tangent to the chain wheel. By such an accurate guiding of the rope to the exact axial centre of the bore-hole, wear on the rope and packing will be avoided. With the balancing beam this absolute centring cannot be attained, even with the most accurate erection,

and obviously a pump working from a balancing beam is subjected to a considerable amount of lateral motion.

c. Rope clamps are often the cause of rope breakages, or, should the rope be well looked after, of continual rope repairs.

Generally, far too little attention is given to the construction and erection of the clamps. The fact is often overlooked that the pump rod, which consists of a solid piece of metal, and the rope, which consists of many wires, probably not less than forty-two, require to be treated very differently. A rod is a solid piece of plant, whilst a rope is a delicate machine.

Owing to faulty construction of the clamps, *e.g.* metal too hard, or unequal pressure from the screws, individual wires are very often crushed and broken, and the rope thereby weakened. Under such conditions the rope will soon collapse. An example of a rope clamp which will not damage the rope is shown in Fig. 5.

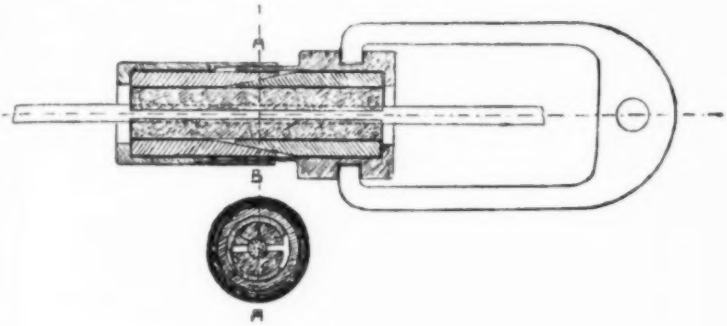


FIG. 5.
CLAMPS.

The rope should be held in a pair of jaws made of hardened rubber or very soft bronze. The jaws are pressed together by a pair of conical split rings made of spring steel, which bring the two stuffing-boxes together by means of screws, and thus the rubber or bronze dies are pressed against the rope. By this arrangement, an absolutely exact closing of the jaws is guaranteed and the possibility of damage to the rope excluded.

5. The last, and a very important requirement, is to lessen the wear on the rope caused by cutting into the tubing in the case of crooked wells. Figs. 6 and 7 show two guides which have given good results.

The first is very simple, and consists only of a bronze cross which is clamped on to the rope. This guide, however, can hardly be used with very crooked holes, as it wears away too quickly, and the bronze dust, which is rubbed off, falls into the well, settling between the plunger and the cylinder, and interfering with the working of the pump.

The second, the Colrol apparatus, although somewhat more costly, is preferable. It consists of steel rollers which revolve with the upward and downward motions of the rope. The guides are placed on the rope

at the parts where the tubing is crooked, and are given more or less play according to circumstances.

It is important to establish exactly where the guides should be placed, and it must be borne in mind that these points may shift from time to time with changes in the condition of the casing. Generally, cut places are indicated by the plunger getting stuck, and should this be noticed

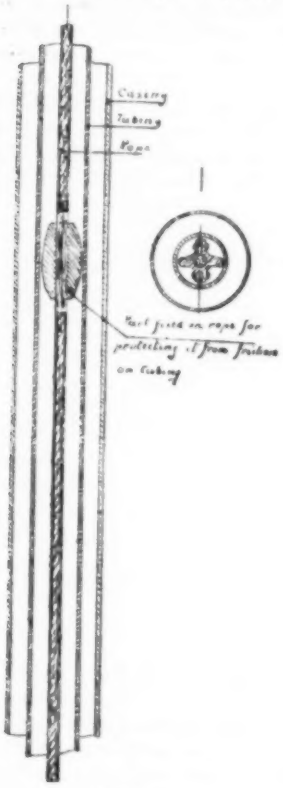


FIG. 6.
SOLID GUIDE.

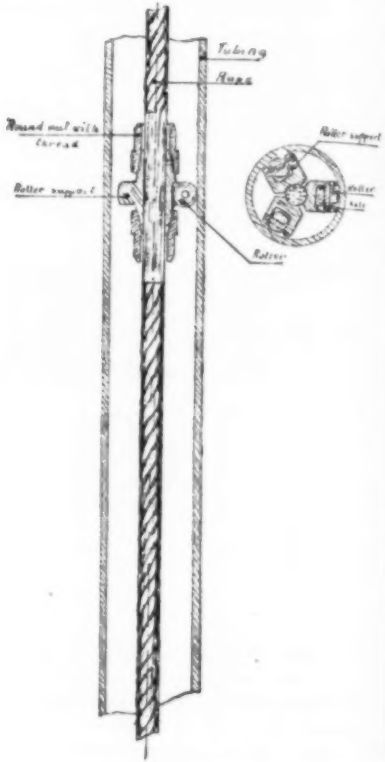


FIG. 7.
COLROL GUIDE.

in time the tubing should be taken out; otherwise the rope will probably break.

When the rope is taken out of the well the worn parts will no doubt show clearly where rope guides are required. Guides can also be used in normal, straight wells, in order to ensure exact centring of the rope in the hole.

The saving of time effected by pumping with the rope is particularly noticeable when pumps are not worked by a separate apparatus, but from a central pumping rig. In such cases to extract and lower the

plunger it is sufficient to put a tripod over the well, and the haulage of the rope can be done by means of a caterpillar tractor provided with a winding drum.

Wire Rope Construction.

The rope must have the following qualities:

1. A minimum of elongation tendency.
2. A minimum of rotating tendency.
3. Stiffness.
4. Resistance to abrasion.

The production of a rope to answer all these requirements has been a problem for the wire rope manufacturer, but great strides have been made towards reaching the ideal.

1. *Elongation.*—This is perhaps the most difficult problem of all, but in the types of rope recently produced, in which there is a minimum of vegetable fibre, elongation has been reduced considerably. There is a multi-strand rope, made entirely of wire, but its use has not been found altogether satisfactory.

2. *Non-rotation.*—This can be obtained partly by:

a. Preformation, or

b. By the multi-strand rope with layers of strands laid in opposite directions.

3. *Stiffness.*—This can be obtained by the reduction of the quantity of vegetable fibre in the rope, and the use of English or Swedish acid steel wire in large diameters.

4. *Resistance to Abrasion.*—For this purpose English or Swedish acid steel wire of large diameter is the best.

DISCUSSION.

Mr. Gwyn Elias referred to sand trouble in wells, some wells being so bad in this respect that even the most careful supervision would not ensure freedom from sanding up of pumps. In such a case it was usual to unscrew the rods, pull up the tubing to the point where the rods unscrewed, again unscrew rods, again pull up tubing to the point of unscrew, and so on until the pump is extracted. Such an operation could not be performed when a well is pumping on a wire line, so that rods in this case would have an advantage.

The tendency nowadays is to use insert pumps to a large extent, and it is of course necessary to ensure that the pump is set properly. It might be more difficult to do this with a wire line, but probably this difficulty could be overcome by using a suitable sinker above the pump.

The pumping of wells in Rumania is now going through a new phase. During the period 1927–1930 many wells were put on the beam, but mostly wells of not greater depth than 1000 metres. From 1930 onwards there was no general advance towards pumping deeper wells until about the beginning of 1933, when a new phase commenced, *i.e.* of pumping deeper wells, down to 1500 metres or more. Depth was not the only

difficulty, as there were also the attendant troubles associated with Mcotic wells, viz. gassy and paraffinous oil.

The gas and paraffin difficulties were not so serious as was at first supposed; the greatest attention had to be paid to overcoming rod and tubing stretch, which was done by using small-bore insert pumps, larger rods near the surface and tubing anchors. Production engineers have been so concerned with these problems recently that they have neglected the possibilities of wire-line pumping.

A great question is the avoidance of undue stretch in the rods or wire line; an effective stroke at the pump is essential.

The case of a well in the Oklahoma City Field is worth mentioning. This was working with a 42-in. stroke at the polished rod, but, as it was adequately proved later, with no movement whatsoever at the plunger. It would be interesting to know how the stretch of a wire line would compare with that of corresponding rods in a pumping well.

No doubt wire-line pumping can offer some advantages, but, as it has probably a technique of its own, it would be advisable to start wire-line pumping at shallower wells.

Mr. J. L. Chaillet said he would like to know whether it was understood that the rope guides would be in the way when the pump is raised, and that therefore during such process the guides would have to be removed.

Mr. E. K. Wallen remarked that he did not consider that any of the packings mentioned in the paper could be really satisfactory; the wire line would cut them away in no time. He recommended the oil-saver, which was a cable-tool appliance, and consisted of a tube, polished on the outside, having a clamping device and stuffing-box on the top, and would pass freely over the whole length of the wire-line. The stuffing-box on the pump tubing was made to fit the outside of this polished tube or plunger, and in lowering the pump valves and sinker-bar, this plunger was retained in the stuffing-box on the tubing at the well mouth. The line passed through it, until the valves were set in the working-barrel and spaced ready for pumping; then the plunger was clamped on to the wire-line and the stuffing-box packed. Any packing would do, as it remained stationary on the wire line. Then the beam was set in motion, and the plunger would be working through the stuffing-box on the pump tubing in the same way as the solid polished rod used in rod pumping. It is thus not necessary that the stuffing-box packing should stand the severe wear and tear of the wire line working against it.

Mr. Leslie Forster pointed out that, in the United States, hickory wood guides were used with great success with rods. The advantage of hickory wood as a material for guides was that it did not drop fragments in the well, and he thought that it could be applied equally well to rope guides.

Mr. Percy R. Clark, in reply, said: In regard to trouble arising from the sanding up of wells, manufacturers of rope pumping equipment had

developed an apparatus called the pull-off sub. It consisted of two parts held together by copper rivets of a much lower tensile strength than the wire rope. Thus, in the event of the plunger being sanded up, sufficient tension was put on the rope to break the pull-off sub in two, and the rope was extracted without having suffered any harm.

In regard to the Oklahoma well, which was working with a 42-in. stroke but had no movement at the plunger, in dealing with the wire rope one must distinguish clearly between elongation and elasticity. Elongation was a permanent change in the rope, and might be regarded as a vice. Elasticity, on the other hand, was a dynamic quality, and could be considered a virtue. There was an extraordinary illustration of this stretch some time ago, when, in drilling a shaft at a mine, the bit came through the roof of a gallery, and one was able to observe the action of the wire rope. It transpired that the bit, when left to move freely in the open gallery, made a stroke some 20 feet longer than that transmitted above. One was thus hardly justified in fearing that in the case of rope pumping any length of stroke will be lost at the plunger.

Guides are made to fix on and take off easily. In the case of guides near the lower end of the rope, these might perhaps be left in position when pulling up the plunger, providing that the winding of that part was done slowly and carefully.

Mr. L. F. W. Schropp, in reply, said: In some wells the sanding up of the pump cannot be prevented, notwithstanding the use of the gas anchor and sand valve. On the other hand, there are some types of pumps which can deal with a certain amount, *e.g.* the fluid packed pump. But even this pump could handle only a small quantity of sand, and he had seen a good many fluid-packed pumps sanded up. Whatever pump was used it was necessary to provide against sand trouble. It was clear that in the case of the sanding up of the well, rods are easier to manipulate than a wire rope; rods can be unscrewed and removed one by one together with the tubes. Nevertheless there are ways of saving the wire rope in the event of the plunger being sanded up, *i.e.* it need not be cut into small pieces when extracting the tubes. It often happens in Copaceni, where he was working, that a swabbing rope or the swab gets stuck in the well. Then the position is the same as with a stuck pump plunger. The rope is pulled up together with the tubing, but was only cut every two or three hundred metres. This meant perhaps a greater loss of time than would occur in the case with pump rods, but it was possible at least to splice the three or four pieces of rope together again.

Mr. Clark referred to the pull-off sub. In a similar manner one could so fix the rope in the rope socket that at a harder pull it would break off there. A third possibility was to construct some instrument to cut the rope above the sinkers. He rather feared it would be difficult to manipulate a mechanical knife in small tubes, but no doubt an electric cutter could be adapted. In any case, one could reckon that, even in sandy wells, sucker rods could be replaced by wire ropes.

The principal thing, however, was to provide against sanding up, and this was quite possible in most wells:—

1. By long slow pump strokes.

2. By using long gas anchors with sand valves, where the sand had time and place to deposit, and,

3. By exact control of the well. Before installing the pump the condition of the well should be ascertained by bailing, *e.g.*

a. The level of the liquid,

b. How much can be pumped without lowering the level, and

c. How much can be pumped during 24 hours without sand coming in.

When these three points had been exactly established, it would no more be difficult to provide against the sanding up of the pump.

The use of insert pumps was not excluded, even when working by rope, but care must be taken to have as long a stroke as possible.

Generally speaking, providing the wire rope had a metal core instead of a hemp one and was otherwise of rigid construction, there could not be much difference between the elasticity of rods and ropes. When extracting the rope it was not necessary to take the guides off entirely: the bolts need only be loosened so that the rope could slide through them, and the guides stacked above the rope socket and taken off together. Larger numbers of guides were used only in exceptional cases, *i.e.* in very crooked holes; generally one worked with only three or four guides. Guides of hard wood should be a very practical proposition. They had the advantage that splinters would float on the liquid, and thus come out of the well together with the liquid, whereas metal dust sank below and jammed the plunger. The oil saver should be very practical, and it might be mentioned that the clamps shown in Fig. 5, by a suitable prolongation of the lower part, could, to all intents and purposes, be changed into a polished tube.

IMPROVED METHOD OF EXAMINING MINERAL OILS, ESPECIALLY THE HIGH-BOILING COMPONENTS, II.*

By J. C. Vlugter, H. I. Waterman, and H. A. van Westen.

Introduction.

In a former paper † the authors have described a new method for the analysis of mineral oils of high molecular weight. This method is based on a complete non-destructive hydrogenation of the oil to be examined. As a means for controlling the absence of aromatic rings in the hydrogenated product the specific dispersion may be used. In the following the properties of this physical constant will be discussed in detail.

The Specific Dispersion as a Means for the Detection of Aromatic Rings and other Unsaturated Compounds in Hydrocarbon Mixtures.

The specific dispersion is the difference between two refractive indices, determined at different wave-lengths of the light, divided by the specific gravity : *e.g.* $\frac{n_{G'} - n_C}{d} \times 10^4$.

This expression can be considered as the difference between the specific refractions according to the Gladstone and Dale formula for the G′-line and the C-line and can therefore be written

$$\left(\frac{n_{G'} - 1}{d} - \frac{n_C - 1}{d}\right)10^4.$$

As the specific dispersion represents the difference of two specific refractions, it is better to use the formula of Lorentz–Lorenz :

$$\left(\frac{n_{G'}^2 - 1}{n_{G'}^2 + 2}\,\frac{1}{d} - \frac{n_C^2 - 1}{n_C^2 + 2}\,\frac{1}{d}\right)10^4,$$

as, for saturated compounds, this can be calculated from the atomic refractions.

Eisenlohr ‡ has determined not only the atomic refractions for the D-line, but also for the C, F, and G′-line of the hydrogen-spectrum. He gives the following values :—

Table I.

	Atomic refractions.				Difference.
	C.	D.	F.	G′.	G′ − C.
For the CH_2-group .	4·5977	4·6178	4·6681	4·7102	0·1132
For carbon . . .	2·4129	2·4180	2·4375	2·4655	0·0564
For hydrogen . .	1·0924	1·0999	1·1153	1·1224	0·0289

* Paper received December 27th, 1934. † *J.I.P.T.*, 1935, **21**, 661.
‡ F. Eisenlohr, *Z. physik. Chem.*, 1910–11, **75**, 600–602.

TABLE II.

Specific Dispersions of Aromatic, Naphth

	t.	$d^t/4$.	n_C^t.	$n_{G'}^t$.	$(n_{G'} - n_C)10^4$.	$\frac{(n_{G'} - n_C)10^4}{d}$
Benzene and derivatives :						
Benzene	25	0·8737	1·49330	1·52014	268·4	307
Toluene	16·4	0·8684	1·49365	1·51970	260·5	300
o-Xylene	15·5	0·8837	1·50368	1·52958	259·0	293
Ethylbenzene	14·5	0·8708	1·49423	1·51904	248·1	285
Mesitylene	17·1	0·8646	1·49403	1·51891	248·8	288
1 : 2 : 3 : 4-Tetramethylbenzene	16·0	0·9044	1·51621	1·54189	256·8	284
1 : 3 : 5-Trimethyl-2-ethylbenzene	16·35	0·8885	1·50875	1·53376	250·1	281
Naphthalene and derivatives :						
Naphthalene	96·6	0·9641	1·57509	1·62295	478·6	496
2-Methylnaphthalene	39·9	0·9939	1·59499	1·64284	478·5	481
1 : 2-Dimethylnaphthalene	16·35	1·0219	1·61014	1·65976	496·2	485
1-Methyl-2-ethylnaphthalene	15·4	1·0014	1·59422	1·63995	457·3	457
1 : 4-Diethylnaphthalene	13·1	0·9983	1·59005	1·63423	441·8	443
1-Methyl-2 : 4-diethylnaphthalene	13·3	0·9870	1·58549	1·62870	432·1	438
Diphenyl and derivatives :						
Diphenyl	77·1	0·9896	1·58112	1·62538	442·6	447
p-Methyldiphenylmethane	19·3	0·9978	1·56579	1·59804	322·5	323
1-Phenyl-1-*p*-tolylethane	17·2	0·9847	1·56038	1·59192	315·4	320
Monocyclic six-carbon ring naphthenes :						
*cyclo*Hexane	20	0·7787	1·4242	1·4361	119	153
Methyl*cyclo*hexane	20	0·7736	1·42365	1·43561	119·6	155
cis-*o*-Dimethyl*cyclo*hexane	20	0·7822	1·42858	1·44088	122·9	157
1 : 2 : 4-Trimethyl*cyclo*hexane	20	0·7813	1·42909	1·44135	122·6	157
1 : 2 : 4 : 5-Tetramethyl*cyclo*hexane	20	0·811	1·44260	1·45524	126·4	156
Monocyclic five-carbon ring naphthenes :						
*cyclo*Pentane	20	0·7510	1·40383	1·41536	115·3	154
Methyl*cyclo*pentane	20	0·7459	1·40750	1·41868	111·8	150
Ethyl*cyclo*pentane	20	0·7610	1·41612	1·42798	118·6	156
Propyl*cyclo*pentane	20	0·7718	1·42285	1·43474	118·9	154
Monocyclic four-carbon ring naphthenes :						
1 : 1 : 2-Trimethyl-3-*iso*propyl*cyclo*butane	20	0·7598	1·4178	1·4298	120	158
1 : 2-Dimethyl-3 : 4-diethyl*cyclo*butane	20	0·7729	1·4219	1·4338	119	154
Monocyclic three-carbon ring naphthenes :						
1 : 2-Dimethyl*cyclo*propane	20	0·6769	1·36941	1·37997	105·6	156
1 : 2-Dimethyl*cyclo*propane	20	0·6928	1·38023	1·39109	108·6	157
Dicyclic naphthenes :						
Di*cyclo*hexylmethane	19·7	0·8765	1·47475	1·48828	135·3	154
Decaline	18	0·8952	1·47789	1·49154	136·5	152
Paraffins :						
n-Pentane	20	0·62632	1·35581	1·3657 •	99	158
n-Octane	20	0·70279	1·39557	1·4066 •	110	157
n-Decane	20	0·7312	1·4103	1·4217	114	156
n-Undecane	20	0·74025	1·41514	1·4267 •	116	157
n-Hexadecane	20	0·7751	1·4329	1·4450	121	156
Rangoon-paraffin	70	0·7744	1·4312	1·4432	120	155

• Read by extrapolation with the formula of Cauchy

$\left(n = A\right.$

II.

Naphthenic, and Paraffinic Compounds.

$\frac{(n_{G'} - n_C)10^4}{d}$	$\frac{n_C^2 - 1}{n_C^2 + 2} \cdot \frac{1}{d}$	$\frac{n_{G'}^2 - 1}{n_{G'}^2 + 2} \cdot \frac{1}{d}$	Difference in spec. refraction for G′ and C-line.		Literature.
			Calc. from the constants.	Calc. from the atomic refraction.	
397	0·3228	0·3480	*152*	65	Beilstein V (Erg. Band, 4th ed., p. 99.
399	0·3350	0·3499	*149*	67	Int. Crit. Tables VII (1930), p. 40.
293	0·3349	0·3493	*144*	69	,, ,, ,, 43.
285	0·3344	0·3486	*142*	69	,, ,, ,, 43.
288	0·3367	0·3510	*143*	70	,, ,, ,, 47.
284	0·3341	0·3479	*138*	71	,, ,, ,, 51.
281	0·3359	0·3497	*138*	72	,, ,, ,, 55.
496	0·3428	0·3657	*229*	62	Landolt-Börnstein II (5th ed., 1923), p. 980.
481	0·3419	0·3638	*219*	63	Int. Crit. Tables VII (1930), p. 53.
485	0·3393	0·3611	*218*	65	,, ,, ,, 56.
457	0·3389	0·3597	*208*	66	,, ,, ,, 59.
443	0·3381	0·3583	*202*	67	,, ,, ,, 60.
438	0·3398	0·3599	*201*	68	,, ,, ,, 61.
447	0·3368	0·3574	*206*	62	Int. Crit. Tables VII (1930), p. 56.
323	0·3268	0·3420	*152*	65	,, ,, ,, 60.
320	0·3286	0·3436	*150*	66	,, ,, ,, 61.
153	0·3278	0·3358	*80*	81	H. A. van Westen, *Diss. Delft*, 1931, p. 48.
155	0·3296	0·3377	*81*	81	F. Eisenlohr, *Fortschritte der Chem., Physik. und phys. Chem.*, 1924–1926, **18**, 540.
157	0·3293	0·3375	*82*	81	
157	0·3300	0·3382	*82*	81	
156	0·3266	0·3346	*80*	81	Willstätter, *Ber.*, 1912, **45**, 1474.
154	0·3255	0·3337	*82*	81	F. Eisenlohr, *l.c.*
150	0·3304	0·3383	*79*	81	,, ,,
156	0·3298	0·3380	*82*	81	,, ,,
154	0·3298	0·3379	*81*	81	,, ,,
158	0·3315	0·3398	*83*	81	Beilstein V (Erg. 4th ed.), p. 24.
154	0·3287	0·3368	*81*	81	,, ,, ,, 24.
156	0·3337	0·3422	*85*	81	J. Baudrenghien, *Bull. de l'Acad. de Belgique* (1929), p. 76.
157	0·3345	0·3430	*85*	81	
154	0·3211	0·3289	*78*	78	C. (1907), II, 1209.
152	0·3161	0·3238	*77*	78	Int. Crit. Tables VII (1930), p. 53.
158	0·3487	0·3574	*87*	86	Shepard, Henne, and Midgley, *J.A.C.S.*, 1931, **53**, 1948.
157	0·3416	0·3500	*84*	84	
156	0·3391	0·3473	*82*	84	H. A. van Westen, *Diss. Delft* (1931), p. 60.
157	0·3384	0·3466	*82*	83	Shepard, Henne, and Midgley, *l.c.*
156	0·3352	0·3434	*82*	82	H. A. van Westen, *l.c.*, p. 70.
155	0·3344	0·3425	*81*	82	,, ,, ,, 86.

$\left(n = A + \frac{B}{\lambda^2}\right)$, as only $n_{G'}$, n_D, and n_F are known.

The authors are aware that Eisenlohr's method of calculating the dispersion values is not correct.* In the following, the authors have taken the value 0·113 for the dispersion of the CH_2-group and 0·029 for the hydrogen atom.

The specific dispersion for the paraffins C_nH_{2n+2} is

$$\frac{n \times 0{\cdot}113 + 2 \times 0{\cdot}029}{n \times 14{\cdot}016 + 2 \times 1{\cdot}008}\dagger$$

Thus it is possible to deduce equations for the other series (C_nH_{2n}; C_nH_{2n-2}; etc.) and to calculate the specific dispersion (or the number of carbon atoms per molecule) for each molecular weight.

As the influence of the number of C atoms per molecule is not important, the course of the specific dispersion for the different series can be deduced from a few values of n :—

	$n = 20$ (Molecular weight about 280).	$n = 30$ (Molecular weight about 420).	$n = 40$ (Molecular weight about 560).
Paraffins (C_nH_{2n+2})	82·1	81·6	81·3
Monocyclic naphthenes (C_nH_{2n})	80·6	80·6	80·6
Dicyclic naphthenes (C_nH_{2n-2})	79·1	79·6	79·9
Tricyclic naphthenes (C_nH_{2n-4})	77·6	78·6	79·1
Tetracyclic naphthenes (C_nH_{2n-6})	76·1	77·6	78·3
Pentacyclic naphthenes (C_nH_{2n-8})	74·5	76·5	77·4

The specific dispersion is, like the specific refraction, dependent on the molecular weight. With increasing molecular weight the specific dispersion of the paraffins decreases; the monocyclic naphthenes have a constant specific dispersion 80·6. For all other series the specific dispersion increases with increasing molecular weight. Graphically, it can be represented as shown in Fig. 1.

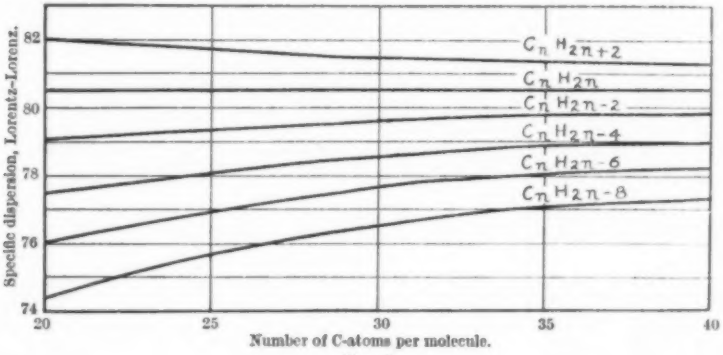


FIG. 1.

* In the Delft laboratory a revision of Eisenlohr's values, using a better method of calculation, is being carried out by Mr. van der Hulst. A paper on this subject has appeared (*Rec. trav. chim.*, 1935, **54**, 518).

† $n \times 14{\cdot}016 + 2 \times 1{\cdot}008$ is the molecular weight of a paraffin with n carbon atoms.

As the specific dispersion is the difference between two specific refractions, the following can be stated: Saturated isomeric compounds have the same specific dispersion (except the small influence of structure differences). This constant value is also suitable for mixtures of hydrocarbons, as it is an additive value. The values for the aromatic and olefinic compounds are much higher than the values calculated from the atomic refractions. The cause of this fact is the increase in the refractive index. Here also, as was the case with the specific refractions, irregularities in the increase of the aromatic compounds can be observed. The position of the rings in the molecule has a great influence on the dispersion. Therefore, it is not possible to deduce a percentage of aromatic compounds or aromatic carbon-rings from the dispersion if little or nothing is known about the type of aromatic compound (naphthalene or diphenyl, etc.).

In one respect, however, the specific dispersion properties differ much from the specific refraction properties. The specific dispersion of the aromatic compounds is much higher than the specific dispersion of the saturated hydrocarbons (paraffins and naphthenes). In the case of the specific refraction the situation is quite different. A high specific refraction is found for the paraffinic and aromatic compounds; only the naphthenes have a low value. This property of the specific dispersion is used in controlling the complete saturation of an oil, that is the absence of aromatic compounds.

In Table II a number of monocyclic and dicyclic aromatic compounds, paraffins, and mono- and di-cyclic naphthenes are collected. The specific dispersion of Lorentz–Lorenz and also the Gladstone and Dale values have been calculated from the physical constants. Also the Lorentz–Lorenz values have been calculated from the atomic refractions. The Gladstone and Dale values are about twice as high as the numbers obtained from the Lorentz–Lorenz formula, which is indicated in Table III.

Consequently, for convenience' sake, $\frac{n_{G'} - n_C}{d} \times 10^4$ can be used.

TABLE III.

	Specific dispersion.	
	Lorentz–Lorenz $\left(\frac{n_{G'}^2 - 1}{n_{G'}^2 + 2}\frac{1}{d} - \frac{n_C^2 - 1}{n_C^2 + 2}\frac{1}{d}\right) 10^4$.	Gladstone and Dale $\frac{n_{G'} - n_C}{d} \times 10^4$.
Benzene	152	307
Some benzene derivatives .	138–149	281–300
Naphthalene	229	496
Some naphthalene derivatives	201–219	438–486
Diphenyl	206	447
Some hydrocarbons with two phenyl nuclei . . .	150–152	320–323
Some naphthenes and paraffins	76–87	150–158

An oil is practically free from aromatic compounds, when the specific dispersion $\frac{n_{G'} - n_C}{d} \times 10^4$ *in hydrogenation or in treating with sulphuric acid has decreased to a value less than* 158.

In 1920 Darmois * already proposed the use of this value. In accordance with more recent literature, he found :—

TABLE IV.

Paraffins C_5H_{11}–$C_{16}H_{32}$	mean 156
Saturated cyclic hydrocarbons C_5H_{10}–$C_{10}H_{20}$.	,, 154
Cyclic olefines C_7H_{12}, C_8H_{14}, and C_9H_{16} . .	,, 190
Aliphatic olefines C_5H_{10}–C_9H_{16}	,, 190
Aliphatic diolefines C_5H_8–C_7H_{12}	,, 225
Homologues of benzene compounds C_6H_6–C_8H_{10} .	,, 300

If the atomic refractions of carbon and hydrogen for the formula of Gladstone and Dale were deduced, for the different wave-lengths of the light, from the known data for a great number of hydrocarbons, it would be possible to calculate the specific dispersion $\frac{n_{G'} - n_C}{d} \times 10^4$ also for the high-molecular saturated hydrocarbons. As the authors had not at their disposal a great number of absolutely pure compounds, these speculative calculations have not been done. It is known with sufficient certainty that, for saturated compounds, $\frac{n_{G'} - n_C}{d} \times 10^4$ has a value between 150 and 158.

The refractive index for the G′-line of a turbid or strongly coloured oil often cannot be determined. Fortunately hydrogenated oils are colourless or only slightly coloured. In this case the formula of Cauchy can be used : $n = A + \frac{B}{\lambda^2}$. This empiric formula gives a linear relation between n and $\frac{1}{\lambda^2}$ (Fig. 2).

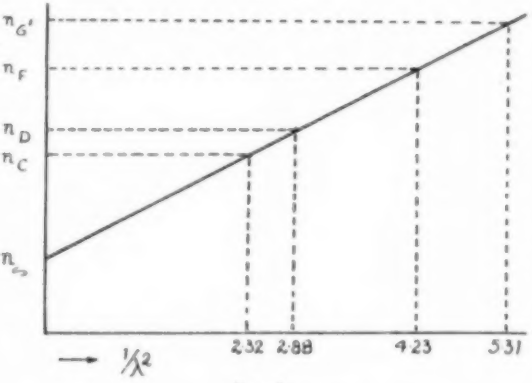


FIG. 2.

Therefore, $n_{G'}$ can be read by extrapolation from the values for n_C, n_D, and n_F. The results are satisfactory as controlled with pure hydrocarbons. It is true that in most cases the points do not lie exactly on a straight

* E. Darmois, *Compt. rend.*, 1920, **171**, 952.

line, but it is possible to determine the $n_{G'}$ rather accurately (four decimals). Other investigators also paid attention to the reliability of this formula.*

TABLE V.

	$\lambda(\mu)$.	$\frac{1}{\lambda^2}$.
C	0·6563	2·32
D	0·5893	2·88
F	0·4861	4·23
G′	0·4341	5·31

Example.—A commercial vaseline-(paraffin)oil was an example of an oil that was apparently free from aromatic compounds, as the ordinary concentrated sulphuric acid (d : 1·84) gives only a very small alteration.

This oil had the following constants :—

TABLE VI.

$n_D^{20} = 1{\cdot}4760$
$d^{20}/_4 = 0{\cdot}8650$
$\frac{n^2 - 1}{n^2 + 2}\frac{1}{d} = 0{\cdot}3261$
Mean mol. weight = 332
Aniline point = 91·0° C.

Assuming that the oil is free from aromatic compounds, the composition can be read from Fig. 1 (the specific refraction–molecular weight graph; compare the preceding paper) for the molecular weight 332 and the specific refraction (r_D) 0·3261 : $C_nH_{2n-1\cdot4}$ ($n = 23{\cdot}5$).

The specific dispersion for a saturated oil of this composition is 79·7. However, there was found experimentally :—

TABLE VII.

$n_C^{20} = 1{\cdot}4733$ $\qquad r_C = \frac{n_C^2 - 1}{n_C^2 + 2}\frac{1}{d} = 0{\cdot}3245$
$n_D^{20} = 1{\cdot}4759$
$n_F^{20} = 1{\cdot}4821$
$n_{G'}^{20} = 1{\cdot}4875$ $\qquad r_{G'} = \frac{n_{G'}^2 - 1}{n_{G'}^2 + 2}\frac{1}{d} = 0{\cdot}3328$

so $(r_{G'} - r_C)10^4 = 83$ and $\frac{n_{G'} - n_C}{d} \times 10^4 = 164$.

The specific dispersion therefore indicates the presence of aromatic compounds.

The treatment with sulphuric acid did not show this. After one treatment (one half-hour's agitating with twice the volume of sulphuric acid with a spec. gr. = 1·84) the constants were :—

TABLE VIII.

$n_D^{20} = 1{\cdot}4753$
$d^{20}/_4 = 0{\cdot}8647$
$\frac{n^2 - 1}{n^2 + 2}\frac{1}{d} = 0{\cdot}3258$
Aniline point = 92·0° C.

* J. F. Eykman, *Chem. Weekblad*, 1906, **3**, 657. F. Th. van Voorst, *Diss. Utrecht*, 1928, p. 101.

However, by a heavy treatment with a mixture of sulphuric acid and oleum (about 10 per cent. SO_3), the following constants resulted :—

TABLE IX.

$$n_D^{20} = 1{\cdot}4680$$
$$d^{20}/_4 = 0{\cdot}8529$$
$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = 0{\cdot}3259$$
Mean mol. weight = 332
Aniline point = 99·0° C.

In this connection it may be remarked that not only aromatic carbon rings are removed, but also naphthenic carbon rings, as the specific refraction goes through a minimum value, while a large amount of sulphur dioxide is formed.

Now the composition is read from Fig. 1 : * $C_nH_{2n-1{\cdot}5}$ ($n = 23{\cdot}5$). The specific dispersion calculated with the formula of Lorentz–Lorenz read in Fig. 1 is 79·6. Experimentally are observed :—

TABLE X.

$n_C^{20} = 1{\cdot}46577$ $\quad r_C = 0{\cdot}3245$
$n_D^{20} = 1{\cdot}46816$
$n_F^{20} = 1{\cdot}47399$
$n_{G'}^{20} = 1{\cdot}47864$ $\quad r_{G'} = 0{\cdot}3323$

so $(r_{G'} - r_C) \times 10^4 = 78$ and $\frac{n_{G'} - n_C}{d} \times 10^4 = 151$.

Now the oil is completely free from aromatic compounds. So in this case a very strong treatment with sulphuric acid was necessary; thus an increase in aniline point of 8° C. was obtained.

Further examples are given in Table XI. From the physical constants given, the specific dispersion value $(r_{G'} - r_C)10^4$ has been calculated and compared with the value calculated from the atomic refractions (read in Fig. 1). The four oils mentioned are completely hydrogenated, as is illustrated by the agreement between dispersion values calculated and found. The oils are arranged in the order of decreasing ring-content.

TABLE XI.

No.	1.	2.	3.	4.
n_C^{20}	1·4977	1·4883	1·4791	1·4753
n_D^{20}	1·5004	1·4909	1·4817	1·4779
n_F^{20}	1·5070	1·4970	1·4877	1·4840
$n_{G'}^{20}$	1·5124	1·5020	1·4927	1·4891
$d^{20}/_4$	0·9246	0·9065	0·8813	0·8666
r_D	0·3183	0·3194	0·3233	0·3266
Molecular weight	352	355	405	525
Formula †	$C_nH_{2n-5{\cdot}1}$	$C_nH_{2n-4{\cdot}4}$	$C_nH_{2n-3{\cdot}3}$	$C_nH_{2n-1{\cdot}8}$
Number of C-atoms	25	25	29	38
$(r_{G'} - r_C)10^4$ found	79	76	78	80
$(r_{G'} - r_C)10^4$ calculated ‡	78	78	79	80

We express our thanks to the Management of the Bataafsche Petroleum Maatschappij for their kind permission to publish this paper.

Delft, The University Laboratory of Chemical Engineering.
December 1934.

* Compare the preceding paper.
† Read in Fig. 1; compare the preceding paper. ‡ Read in Fig. 1.

THE REFINING OF A CRACKED MOTOR SPIRIT.*

By D. Glynn Jones, M.Sc., M. Am. Assoc. Pet. Geol.
(Associate Member.)

SYNOPSIS.

The paper is mainly an account of the vapour-phase refining of a cracked motor spirit produced in the Argentine. Gas oil is the present charging stock to the cracking plants, but a brief summary of the results of cracking other earlier charging stocks is given. Details are included of the manufacture of the clay, its laboratory evaluation, and of the operation of the cracking plants, Gray towers and treating plant.

Comodoro Rivadavia crude oil is a heavy crude containing very little of the petrol and kerosine fractions. In character it varies slightly from one part of the field to another, but its general analysis may be given as :

Table I.

Specific gravity at 15° C.	0·960
Saybolt Furol viscosity at 50° C.	325 sec.
Water	25 to 40%
Paraffin Wax	1·2%
Hard Asphalt	0·05%
Soft Asphalt	16·0%
A.S.T.M. Distillation.	
Initial Boiling Point	250° C.
Off at 300° C.	4%
Off at 320° C.	7%
Ultimate Analysis of Dry Crude.	
Carbon	86·43%
Hydrogen	11·86%
Oxygen	1·04%
Nitrogen	0·41%
Sulphur	0·18%
Ash	0·08%

In the light of this analysis it is obvious that cracking must be resorted to for the production of gasoline. This is done by the Cross cracking process, the plant consisting of two 1000-barrel hot-oil units. At present a gas oil derived by a low-pressure crack of the crude is used as a charging stock, but other charging stocks have been employed in the past.

The Cracking Process.

Gas oil of specific gravity 0·890, preheated in the coils of the bubble tower and evaporator, is fed into the lower section of the bubble tower, where it is stripped of its gasoline fraction and thence, together with the

* Paper received Jan. 9th, 1935.

recycle stock, flows by gravity to the "mixing tank" or accumulator (see Fig. 1).

It was found that less gasoline was charged to the furnaces by this arrangement than by the introduction of fresh feed to the mixing tank itself. The hot-oil pumps take suction from the mixing tank and circulate the charge through the cracking system of reaction chamber, evaporator (where recycle stock, gasoline and fixed gases are flashed off the heavy residue), back to the bubble tower, which fractionates out the gasoline and fixed gases from the recycle stock.

Gasoline vapours and gas pass overhead to the Gray tower system as described below. Other streams entering the bubble tower are: (1) Reflux gasoline, which consists of gasoline derived from the Kellogg low-pressure cracking plants, and off-specification gasoline which requires

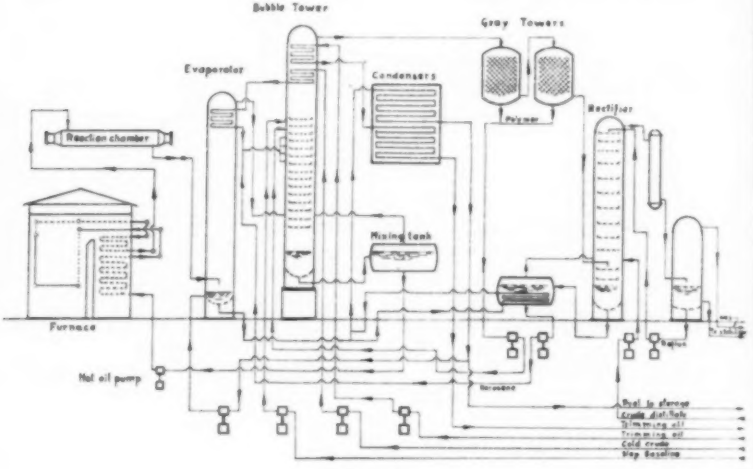


FIG. 1.

FLOW DIAGRAM.

redistillation; (2) Polymers from the Gray tower system; (3) Gasoline-stripped crude distillate which is the product obtained by a flash distillation of the crude oil in Foster topping units.

Pertinent details of the operation of the Cross units are tabulated below. Throughputs are based on one unit, the actual daily throughput being approximately twice the volumes shown. The material balance is struck for the whole of the system, including the stabilizer, which processes a mixture of absorption plant gasoline and cracked gasoline to a minimum of 97 per cent. recovery.

THE REFINING PROCESS.

The gasoline produced by the cracking plant bubble tower is corrosive, has a bad colour, high gum content and the very disagreeable odour

TABLE II.

Material Balance.

(Figures based on one unit.)

	M³ in 24 hours.	Brls. per day.	Sp. gr. at 15° C.	Total lb. per hour.	Per cent. by weight.
Streams entering System.					
Gas oil	149	938·0	0·889	12,150	
Crude distillate	26	163·5	0·817	1,942	
Reflux gasoline	36	226·0	0·810	2,680	
Absorption gasoline to stabilizer	11	69·2	0·680	687	
Total feed				17,459	
Streams leaving System.					
Total * gasoline	115	724·0	0·740	7,800	44·5
Polymers	20	125·8	0·845	1,550	8·9
Residue	65	409·0	1·000	5,960	34·0
Gas, stabilizer	1,700			203	1·5
Gas, cracking plant	10,000			1,192	6·8
Unaccounted for				755	4·3

NOTE :—

(*a*) It is calculated that the net yield of cracked gasoline is 87 M³, or 547 brls.
(*b*) Total gas per barrel of *total* * gasoline = 566 cubic feet.
(*c*) Cracking plant gas per barrel of *cracked* gasoline = 640 cubic feet.
(*d*) Percentage yields by volume on the charge are :—

Cracked gasoline	49·9%
Residue	37·5%
Polymers	4·6%
Loss (gas and coke)	8·0%

(*e*) The normal recycle ratio of recycle stock to fresh feed charged to the furnace is 3·8 to 1.

* *Total* gasoline includes cracked gasoline, refluxed gasoline, stabilized absorption plant gasoline, and gasoline introduced in charging stocks.

TABLE III.

General Operating Temperatures, Pressures, etc.

	Temperature, ° C.	Pressure, lb./in.².
Fresh feed to bubble tower	200	140 (at pump)
Mixing tank	295	44
High-pressure pump	—	1,100
Reaction chamber	475	825
Evaporator, bottom	375	48
,, top	350	48
Bubble tower, bottom	300	50
,, ,, top	180	50
Gray towers, inlet to 1st	170	45
,, ,, outlet to 2nd	173	35
Rectifier, bottom	240	—
,, top	155	—
Gas separator	15	30
Stabilizer, bottom	165	104
,, top	40	104

Average length of run = 690 hours.
Longest individual run to date = 2,708 hours.

associated with the presence of hydrogen sulphide, mercaptans and other sulphur bodies, etc. To render the spirit suitable for marketing, (1) gum content must be reduced and the colour improved, (2) corrosivity must be removed and the odour improved, (3) the spirit must be processed to a satisfactory recovery.

The first part of the refining is brought about by the Gray vapour-phase process, the gasoline afterwards being stabilized and treated with a lime wash followed by a water wash. The resulting motor spirit has the following analysis :—

TABLE IV.

Specific gravity at 15° C.	0·745
Colour, Saybolt chromometer	30 plus.
Gum content, copper dish	1 to 5 mgms./100 ml.
Initial boiling point	32° C.
Recovery at 100° C.	34%
End point	200° C.
Recovery	97%
Vapour pressure (Reid)	6 lb.
Doctor test	Lightly positive.
Corrosion	Nil.
Octane No. (C.F.R. Motor Method)	74
Aromatics and olefines	29·5%
Naphthenes	41·5%
Paraffins	29·0%

Vapour-phase refining.—The Gray process consists in passing the hot gasoline vapours downwards through a mass of contact material of fuller's-earth type contained in a " catalizer." The issuing vapours are condensed in a separate condenser, while colouring matter and polymers which condense in the chamber itself are drawn off in the liquid phase from a separate outlet. The contact towers used at the Comodoro Rivadavia refinery are five single-shell 11-feet diameter towers of a nominal 16 tons fuller's-earth capacity, the clay being held on a perforated plate covered by a monel-metal screen of 40 mesh. By changing the vapour inlet from the shoulder of the towers to the charging manhole at the top, the capacity of the towers has been increased to about 28 tons of local clay per charge.

Gasoline vapours, then, enter the contact towers above the bed of clay, pass downwards, and are drawn off about 1 foot below the perforated plate. Thence they pass to a twelve-tray rectifying column with reboiler, which removes entrained polymers and serves as a convenient control of end-point variations. Polymers are drained off at the lowest point of the catalizer and are recycled to the cracking system. The whole process is under the charge of the crew operating the Cross units.

RESULTS WITH EARLY CRACKING STOCKS.

(a) *Kerosine.*—The first charging stock employed was kerosine made by a straight distillation of Comodoro crude, which contains some 5 per cent. of this material. The kerosine has an initial boiling point of 15° C., end point of 320° C. and specific gravity 0·865, and was cracked at 470° C. under a pressure of 750 lb./in.^{2}, the Gray towers being charged with 13 tons of North American fuller's earth.

The gasoline from the bubble tower had a Saybolt colour of + 2 and

copper dish gum content of 1200 mgms. per 100 ml. After treatment in one Gray tower the spirit had a colour of better than + 25 Saybolt and a gum content of 275 mgms. The spirit proved colour stable, retaining its colour in tanks and for at least three months when stored in glass bottles in daylight. The gum content, however, was excessive and the gasoline was corrosive and malodorous. One ton of fuller's earth treated 230 M^3 of this gasoline to a colour of + 25. The colour then dropped to + 24 and finally to + 21. Attempted regeneration of the catalyst by steaming and blowing down with gasoline vapours was unsuccessful.

(b) *Topped crude.*—Owing to the small volume of kerosine available for cracking, attempts were made to crack the crude oil itself after the removal of the light fractions. The topped crude has the characteristics: Specific gravity 0·942 at 15° C., and viscosity Saybolt Furol of 300 to 350 sec. at 50° C.

This stock, cracked at 460° C. and 750 lb./in.^{2}, yielded 10 to 12 per cent. of 200° C. end-point gasoline, amounting to about 35 M^3 per day. After a contact-treatment similar to that of the gasoline obtained by cracking kerosine, the product had a better colour than + 25 Saybolt and the comparatively low gum content of 25 mgms. An immediate alkali wash was thought to have produced a satisfactory cracked gasoline. However, the spirit was found to be unstable. Colour rapidly changed during storage in tanks, and the further handling involved in transfer from one tank to another caused the colour to deteriorate still more, until finally the gasoline had a distinct primrose-yellow colour. Samples of the spirit stored in the dark dropped from + 25 to + 22 in two weeks. Samples exposed to sunlight dropped to + 19 after twelve hours. Treatment with caustic soda, sodium hypochlorite, sodium plumbite and sulphur accelerated the deterioration. However, on redistillation it was found that most of the colouring matter remained as a residue.

The effect of a second vapour-phase treatment was next tested, gasoline ex fuel oil being used as wet-trim in the bubble towers while kerosine was being cracked. The fuel oil gasoline, therefore, passed twice through the contact towers. The composite spirit so obtained was not stable to sunlight, colour dropping from + 25 to + 23 in four hours. Nevertheless, the material was colour stable for at least two months in tanks and also survived the transference from tanks to tankers. For some time, therefore, this method of re-running was adopted, the stock of kerosine being sufficient for this purpose.

(c) *Gas oil.*—Somewhat later, in order to obtain a higher gasoline yield from the crude oil, two Kellogg pressure pipe stills were installed. Imposing a slight crack (450° C.; 250 lb./in.^{2}) on topped crude these two stills now yield some

7·5% of gasoline (sp. gr. 0·750).
41·3% of gas oil (sp. gr. 0·890).
49·2% of heavy residue (Saybolt Furol Viscosity at 50° C. of 1700 sec.).
2·0% of loss as gas, etc.

The gasoline, which has an average Saybolt colour of + 4 and a high gum content, is used as part of the wet-trim to the cracking plant bubble

towers. The gas oil is the charging stock to the cracking plants and has been somewhat improved since the early operation of the plant by the elimination of almost all its gasoline content. The heavy residue obtained is cut back with Cross residue to give a marketable fuel oil.

The gas oil obtained from these units is cracked in the Cross plants at 475° C., and yields some 70 M^3 per day per plant of gasoline similar in its colour instability to that obtained by cracking topped crude. Samples of the gasoline taken from the run-down stream after passing through one Gray tower were stored in glass bottles in the dark. The colour of the gasoline, without any further treatment, dropped from + 30 to + 22 in three days. Treatment with the ordinary refining agents such as caustic soda, sodium hypochlorite and 1 per cent. by volume of sulphuric acid, rendered the spirit even more unstable. This gasoline, however, now formed the greater part of the production and hence could not be redistilled as wet-trim while cracking kerosine.

Attempts were therefore made to give it a double vapour-phase treatment. For this purpose the vapours were passed through two Gray towers connected in series, each being charged with 12 tons of fuller's earth of 30 to 80 mesh. The yield of + 30 colour gasoline obtained by this treatment was 45 M^3 of gasoline per ton of catalyst, amounting in all to 1080 M^3 of gasoline per charge. The product had a low gum content, was colour stable in tank storage for over three months, and when the catalyst was comparatively new, the gasoline could be exposed to sunlight without any change in colour.

As a further confirmation of the efficacy of the series treatment, an alkali-washed sample of gasoline from the second Gray tower was stored in a vented iron drum over a period of four months. During this time the colour dropped from + 30 to + 23, and gum content increased from 40 mgms./100 ml. to 82 mgms. Much of the deterioration was undoubtedly due to evaporation,* since the initial boiling point rose from 25° C. to 98° C., and the specific gravity from 0·740 to 0·780. However, these results were considered sufficiently satisfactory to warrant the installation of further towers, sufficient to carry out the series treatment on all the cracked gasoline produced.

Employment of Local Clay.

Having achieved a reasonably satisfactory gasoline by vapour-phase refining, an attempt was made to cheapen the process by substituting a local clay for the expensive North American fuller's earth. Preliminary experiments were made in a miniature glass Gray tower; these proving satisfactory, development was made via a small-scale tower to an actual run on the Gray towers themselves, a sufficient quantity of local clay of 30 to 60 mesh being obtained for this purpose. The experiment proved highly satisfactory, and although local clay treats only 20 M^3 of gasoline per ton of charge as compared with 40 M^3 for fuller's earth, the economy resulting from its use is considerable. The saving amounts to approximately $4 (Argentine) per ton of cracked gasoline.

* An actual evaporation of 60 per cent. had taken place.

Using the series treatment and employing local clay, more than 120 M^3 of gasoline per day per cracking plant can be treated, the vapours passing through some 56 tons of clay. The product (after passing the rectifiers) has a copper dish gum content of less than 5 mgms. per 100 ml., this figure being held up to a yield of approximately 20 M^3 gasoline per ton of clay. Moreover, the spirit is colour stable, dropping to not lower than + 28 from an initial + 30 Saybolt after two hours' exposure to sunlight and overnight storage.

Preparation of the Clay.

The local clay used to replace fuller's earth in the Gray towers is a soft friable grey clay, being a volcanic tuff of Eocene age. Its chemical analysis is as follows:—

Table V.

Density	2·3
Silica (SiO_2)	65·10%
Ferric oxide (Fe_2O_3)	4·98%
Alumina (Al_2O_3)	15·74%
Calcium oxide (CaO)	2·56%
Magnesium oxide (MgO)	2·10%
Loss on calcining	5·84%
Alkalis (by difference)	3·68%
	100·00%

The clay occurs in a hill 200 feet high, and having a circumference of about $\frac{1}{2}$ mile. The factory is situated at the foot. Clay is removed from the hill by blasting, and carried to the end of a belt conveyor (1 ft. wide) by means of a bucket excavator. The few lumps larger than 1 ft. to 1 ft. 6 in. size are broken with picks and the clay then manually shovelled on to the belt conveyor, of which the other end overhangs a jaw crusher. This machine takes lumps up to 1 ft. to 1 ft. 6 in. in size, reducing them to a maximum of 2 in.

The crushed clay is delivered to a bucket elevator which feeds it into a parallel flow rotary drier, 5 ft. diameter and 40 ft. long. This is heated by the combustion of natural gas in two burners built into a Dutch-oven type of setting. Flue gases and clay dust are extracted at the other end by an electrically driven fan, discharging to the air through a cyclone collector. The cyclone collector traps a certain amount of the coarser material in the dust, but at the same time there is a high loss as dust vented from the top of the chimney. The temperature of the rotating drier varies from about 300° C. at the furnace end to about 70° C. at the extraction end. The clay is moved along by deflecting blades mounted inside the drum in the form of a discontinuous spiral, aided by the slight inclination of the drum itself.

At the outlet end of the drum the dried clay drops through a shute to a bucket elevator which delivers the clay to two hammer mills in equal portions. In these the clay is further pulverized to a size below $\frac{1}{8}$ in. in diameter, and then passed to a further system of elevators delivering the pulverized clay to one of three rotating screens, or trommels. These are built in sets of two. The top screen is of 20 mesh, and the lower screen of 80 mesh. From the top screen of each pair, particles of clay larger than

20 mesh are recycled to the hammer mills, and particles of smaller size are conveyed by a screw working in a trough to the lower screen in which dust is rejected and the product (20 to 80 mesh) delivered to an elevator which conveys the clay to storage bins.

In order to minimize the dust in the atmosphere two exhaust fans are installed. One (of 15 H.P.) works on the revolving oven and the two hammer mills, the other works on the classifiers. It has been found that 20 tons per day of dust are eliminated by these fans. Dust from the bottom of the classifiers and from the cyclone collector drops into a series of water channels whence it is washed out to sea.

In the development of this plant the best possible use has had to be made of the materials locally available. For this reason the yield of finished product based on the throughput of raw clay is low, the plant normally working with a yield of 20 per cent., but the existence of a satisfactory market for the fines would bring about a big saving in the cost of producing the clay.

The following table (see also Fig. 2) shows the process of comminution of the clay traced through the various stages.

TABLE VI.

(The figures refer to weights in tons, and are based on a throughput of 100 tons of raw clay.)

	Rotatory Oven.		Hammer Mills.		Classifiers.	Product.
	In.	Out.	In.	Out.	In.	
Coarse . .	88·0	77·5	77·5	15·7	15·7	2·6
20–80 mesh .	5·0	5·0	5·0	30·3	30·3	17·4
Fines . .	7·0	2·5	2·5	28·0	28·0	2·0

It appears that the hammer mills are too drastic a process of trituration for the clay employed. A mill of the rotary crusher type or a ball mill would probably be more suitable. Similarly, a vibratory screen would reduce considerably the loss of valuable product through a degradation to dust. However, taking into consideration the available equipment, the plant works very efficiently.

The clay plant being situated at a distance of 5 kilometres from the refinery, transportation has been somewhat difficult. Originally clay was filled into sacks, loaded on to trailers and brought down to the refinery by tractors. At the refinery the sacks were lifted to the level of the top of the Gray towers by a winch and emptied by hand. Since the installation of a large silo alongside the Gray towers together with a system of bucket elevators, clay has been brought down in large metal bins, each holding 8 tons and drawn in pairs by a tractor. Very recently, however, trucks of smaller capacity have been used, each holding 6 tons of clay and drawn by an ordinary motor-lorry chassis specially adapted for attaching a two-wheeled trailer. Whereas the old tractor arrangement required about four hours for the return journey and used a large quantity of spirit, the transport

at present in use requires only one hour for the double journey, and operates at a cost of just over $1 per ton of clay.

Charging and Discharging the Clay.

At the refinery, clay is emptied from the trucks through a bottom draw-off arrangement into a concrete pit. Thence it is picked up by a bucket elevator and emptied into the top of the silo. When Gray towers are being filled the clay is run out from the bottom of the silo into another bucket elevator which conveys it to a height of 20 feet above the top of the towers, whence it is run into the tower concerned through a galvanized-iron pipe of 4 in. diameter.

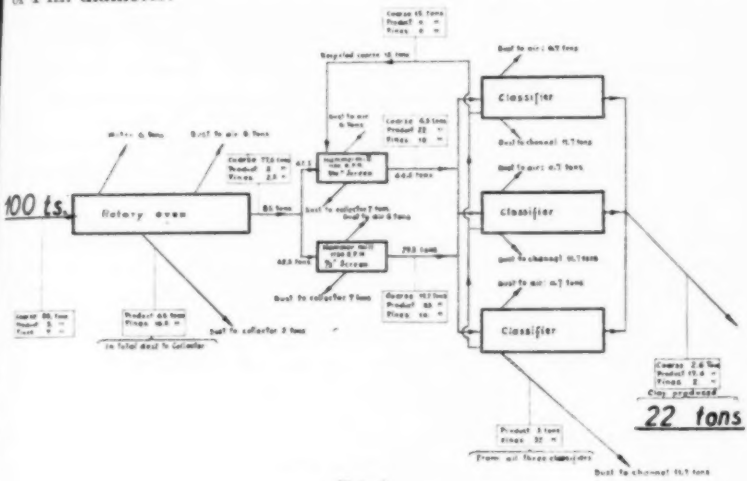


Fig. 2.

Flow sheet of clay plant.

In order to prevent the loss of fine clay through the 40-mesh monel-metal screen at the bottom of the towers, some two feet of coarse (10 to 20 mesh) clay is first introduced, followed by finer clay (nominally 20 to 80 mesh) having the average screen analysis (U.S. Standard sieve series) :—

On 20 mesh	. . . . .	Nil.
20–30 ,,	. . . . .	35%
30–40 ,,	. . . . .	26%
40–60 ,,	. . . . .	27%
60–80 ,,	. . . . .	12%

Clay is filled in up to 1 metre of the top manhole, the manhole is replaced and bolted down, and the tower is then ready for use.

When a tower has been put out of service on account of the gum tolerance having been exceeded, steam is blown through it for a space of 20–24 hours. During the first four hours the steam and gasoline vapours which leave the tower pass through a condenser and thence to a small (50 brls.) run-down tank. Some 6 cubic metres of gasoline are recovered in this way from each filter. When the appreciable evolution of gasoline has

ceased the vapours are turned over to the smoke-stack and steam allowed to blow through for the remainder of the time. To empty the towers the top manhole and the bottom draw-off valve are opened, and as the clay is still free flowing, it discharges into a wooden trough down which sea-water flows, carrying the spent clay out to sea. The spent clay is dark brown in colour and extraction with carbon tetrachloride or other solvents shows it to contain about 2·5 per cent. of extractable material, but as this is of a tarry or resinous nature further cracking would be of little value.

Evaluation of Clays for Use in the Gray Towers.

There are at least two local clays which appear suitable for use in the Gray towers. One is a grey clay, the other a green clay. In chemical composition they do not present much difference. Mechanically one is somewhat harder than the other, giving a better yield when processed in the plant to yield fine clay of the appropriate mesh. On the other hand, this harder clay is more inaccessible and transport costs are excessive. An attempt was made to assess the efficiency of these clays in the laboratory, using North American fuller's earth as a control.

The apparatus employed was a small wide-necked glass bottle, fitted with a cork stopper through which passed a thermometer, a small separating funnel and a wire mixing device. A definite quantity of clay was introduced into the bottle, and its temperature noted. Fifty millilitres of gasoline at the same temperature were poured into the funnel and passed through into the bottle, with constant agitation.

In most cases this was followed by a rise in temperature of the mixture, due to "Heat of wetting." For the first set of results gasoline direct from the Cross bubble tower was used, but comparison with refined gasoline indicated that the difference in temperature rise when the same clay was treated separately with each gasoline was negligible, hence refined gasoline was subsequently employed.

In order to test the efficiency of the clays, the clay was "activated" by maintaining it at a certain temperature over a period of five hours, allowing it to cool, and then testing it in the apparatus described above. A fresh quantity of the same clay was then activated at a different temperature and the test repeated. In each case, comparison is on a volume basis, since it was really desired to know the probable efficiency of a definite volume of clay in the Gray towers. Therefore 60 ml. of clay were tested against 50 ml. gasoline.

The following are some representative results obtained (see also Fig. 3) :—

Table VII.

Temperature of Activation.	Observed Rise in Temperature.		
	Grey Clay.	Green Clay.	Fuller's Earth.
No activation	0·0° C.	0·0° C.	0·7° C.
120° C.	3·3° C.	3·6° C.	4·0° C.
250° C.	4·1° C.	4·7° C.	2·5° C.
300° C.	4·2° C.	5·0° C.	2·5° C.

Up to an activation temperature of 120° C. fuller's earth is the most efficient. When activated above this temperature, however, the efficiency of fuller's earth falls off rapidly, green clay occupying the premier position, which it retains up to 300° C. Above a roasting temperature of 300° C. the activation of green clay falls off rapidly. It appears that the optimum temperature of activation of local clays is 300° C. Furthermore, it was found that there is a marked correlation between the loss in weight on heating to the activation temperature and the activity of the clay. The latter varies directly as the former. These results were checked by distilling gasoline vapours through a known volume of clay in a miniature Gray tower.

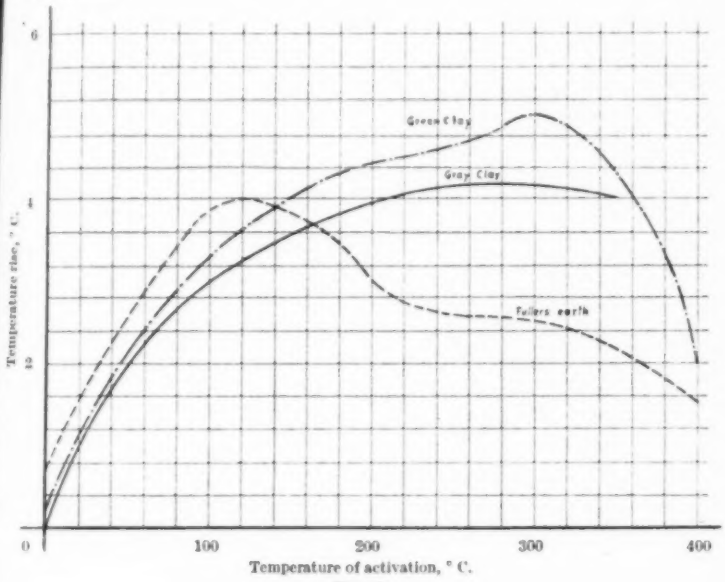


FIG. 3.

ACTIVATION OF LOCAL CLAYS.

Following on these laboratory investigations a protracted run was made on green clay in which the above results were confirmed, viz. that green clay functions better than grey clay, but neither is as good as fuller's earth. However, on account of the comparative inaccessibility of the green clay deposits, its improved performance did not counterbalance the increased cost.

METHOD OF OPERATION OF THE GRAY TOWERS.

The details of the operation of the Gray towers can be best described by following out the history of a freshly-charged tower.

As described above, 3 M^3 of coarse clay (approximately No. 10 sieve U.S. Standard sieve series) is charged into the towers to rest on the perforated monel-metal screens. Above this is introduced a further 25 M^3

of fine-mesh clay (20–80) and the manhole closed. When the tower is put on stream, gasoline vapours passing out of the previous second filter are allowed to enter at the top of the new tower in the space above the clay. The tower being cold, considerable condensation of gasoline takes place at first.

The condensate flows to the polymer accumulators and is continuously pumped off to be recycled in the Cross bubble towers. As the temperature of the Gray tower rises, so the condensation gets less and gasoline vapour eventually pass to the rectifying column and thence to the condenser and gas separator, from which it is sent to a slop tank until laboratory inspection indicates that the gasoline has better than + 30 Saybolt colour. The

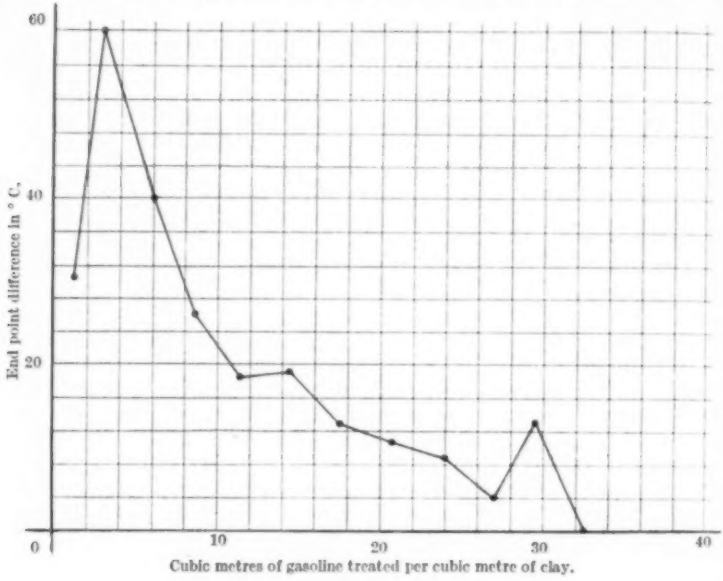


FIG. 4.

RELATIONSHIP OF GASOLINE END POINT TO VOLUME OF GASOLINE TREATED BY CLAY.

stream is then diverted to the stabilizer and the treating plant for processing as specification gasoline. In the meantime the exhausted Gray tower of the set has been taken out of circuit and steaming out will have commenced.

As soon as a steady temperature is attained by the outgoing vapours of the new tower, it is noticed that they are at a higher temperature than the ingoing vapours from the preceding filter. The maximum temperature difference that has been recorded while working with local grey clay is about 15° C. As the amount of gasoline treated by the clay increases, it is found that this temperature increment decreases, until, when the filter is condemned on the basis of the gum content of the outgoing gasoline, there is a drop of 5° C. in the temperature of the vapours passing through the tower. At the same time the end point of the gasoline changes considerably. Fig. 4 is a curve in which the difference between the end point

of the ingoing gasoline and the end point of the outgoing gasoline is plotted against the gasoline throughput of the tower.

This is a typical case, which also shows the slight irregularities in behaviour due probably to temporary variations in the operation of the cracking plant such as slight temperature or pressure changes, variations in the amount of slop gasoline being refluxed to the bubble towers, etc. A plot of the difference in temperature of the ingoing and outgoing vapours follows this curve very closely.

Mention should be made of the water which is expelled from the clay by the gasoline vapours. It has been found that the volume of water that can be definitely traced to the Gray tower is in very close agreement with

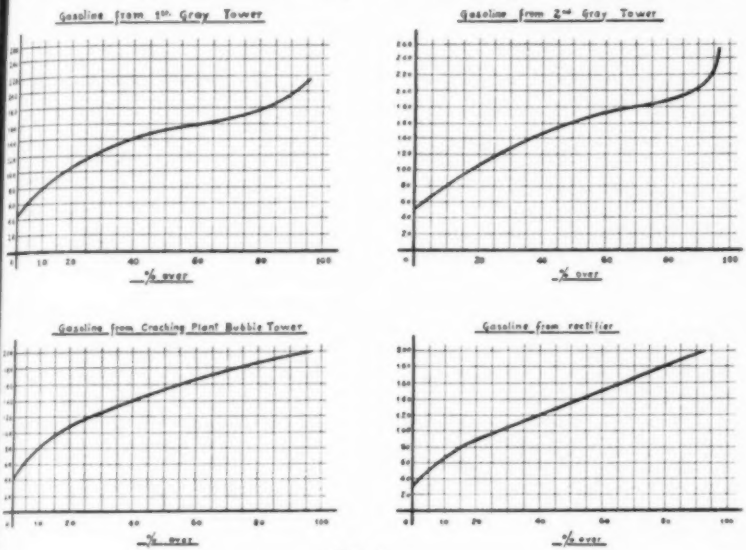


FIG. 5.

GASOLINE DISTILLATION CURVES.

the percentage of moisture present in the clay. The expulsion of water from the clay entails the condensation of gasoline vapours (approximately in the ratio of 8 parts of gasoline to 1 part of water). The volume of polymers is consequently increased. Since the recycling of polymers to the cracking plant always involves a distillation loss, it is clearly advisable to dry the clay as thoroughly as possible before charging the tower.

The reaction going on in the contact towers is one of polymerization of diolefines and other unsaturated hydrocarbons. At the same time the "heat of wetting" which was studied quantitatively in the laboratory is sufficient to raise the temperature of the whole of the contents of the tower, thereby preventing part of the polymerized material from condensing and being removed from the system by the polymer pumps. It is those compounds which cause the heavy ends that are clearly seen in the accompanying curves (Fig. 5), in which are plotted (*a*) the distillation curve of the

gasoline leaving the bubble tower, (*b*) the distillation curve on leaving the first tower, (*c*) the distillation curve on leaving the second contact tower, (*d*) the distillation curve of the gasoline after rectification in a twelve-tray rectifying column with reboiler heated by cracking plant evaporator bottoms.

The set of distillations chosen for the purpose of constructing this curve is typical. The least accurate portion is that adjacent to the initial boiling point, since a high evolution of gas occurring when withdrawing the gasoline sample from the bubble tower and the Gray towers causes some loss of light fractions. However, the relation of the end points is clear. The first filter brings about a slight rise in end point, the second one a further rise, while the rectifier fractionates out the heavy ends brought over from the contact towers and gives the gasoline a reasonably good fractionation curve.

Further analytical details of the particular four samples are as follows:—

TABLE VIII.

	Gasoline from Bubble Tower.	Gasoline from 1st Gray Tower.	Gasoline from 2nd Gray Tower.	Gasoline from Rectifier.
Specific gravity	0·766	0·771	0·777	0·746
Colour, Saybolt	+15	+30	+30	+30
Gum (Copper dish) in mgms./100 ml.	645	575	405	2

From the rectifiers the gasoline passes to a stabilizing unit in which cracked gasoline is blended with absorption gasoline and stabilized to a recovery of 97 per cent.

A series of tests was carried out on the Gray towers over an interval of some months when end point, colour, gum content, etc., were recorded daily. The summarized averages are given below:—

TABLE IX.

Average Results of Working of Gray Towers.

Gasoline from	End Point.	Colour (Saybolt).	Gum.	Increase or decrease in	
				End Point.	Gum.
	° C.		mgms.	° C.	mgms.
Bubble tower . .	198	+12	533	—	—
First contact tower .	206	+26	423	+ 8	−110
Second contact tower .	220	+29	264	+14	−159
Rectifier . . .	200	+30	2	−20	−262

The usefulness of the rectifier following the Gray towers is strikingly shown. In the first place it enables an accurate control to be kept on the end point of the finished gasoline. In this way the variable increase in end point through catalytic action of the clay is taken care of, and also any variation in end point of the gasoline as it leaves the bubble tower. In the second place, it acts as a trap for uncondensed and/or entrained

polymers. The actual control is brought about by an automatically maintained (air activated control working on a gasoline reflux-pump) constant tower top temperature.

The volume of polymers produced depends to some extent on operating conditions, but on the average a throughput of 100 M^3 of cracked gasoline produces about 20 M^3 of polymers, of which some 40 per cent. boils at over 200° C. The normal production of polymers is 4 to 5 per cent. by volume of the gas oil charging stock to the cracking plant, reckoned on a gasoline-free basis. A typical analysis of polymers is as follows :—

TABLE X.

Specific gravity	0·830
Initial boiling point	82° C.
Off at 200° C.	60%
Off at 300° C.	86%
End point	370° C.
Recovery	98%

There is no apparent difference in the polymers as produced by each tower of the pair.

To summarize, it appears from the foregoing that vapour-phase refining in the Gray towers operates as a simple polymerization of gum-forming and coloured constituents of cracked gasolines. These are either condensed in the contact towers in which they were produced and removed by the polymer pumps, or passed on to the rectifying tower as vapours where they are separated from the more volatile end-point gasoline which passes overhead. The polymers and rectifier-bottoms are re-circulated to the cracking plant. Their gasoline fraction passes over again in the vapours to the contact towers, while the heavier fractions join the fresh-feed and re-cycle stock and are re-circulated through the cracking system.

FINAL TREATMENT.

On leaving the gas separator of the rectifying plant the cracked gasoline has + 30 Saybolt colour and less than 5 mgms. of gum, but possesses the low recovery of 93 per cent. and contains free hydrogen sulphide and a high mercaptan content (0·04 per cent. by weight as butyl mercaptan). The gasoline therefore requires stabilizing, the elimination of hydrogen sulphide and the reduction of mercaptan content. It passes then to a horizontal surge tank wherein it is blended with absorption plant gasoline (recovered from field and refinery gases). Thence the blend is pumped direct to the stabilizer, which is a 30-tray column operating at 104 lb. per square inch, a top temperature of 40° C., and a kettle temperature of 165° C. The blend leaves the unit with a minimum recovery of 97 per cent., and free of hydrogen sulphide, which escapes with the fixed gases. These have the following analysis (Podbielniak apparatus) on a hydrogen sulphide free basis :—

TABLE XI.

Methane and fixed gases	12·15%
Ethylene	1·00%
Ethane	15·48%
Propylene	8·38%
Propane	45·66%
*iso*Butane	12·71%
Butane	4·62%

The partial elimination of mercaptans is effected by a lime wash. Thorough mixing of a lime slurry and gasoline is procured by pumping the two liquids through a line fitted with orifice plates. The line discharges tangentially into a settling tank, from the bottom of which lime flows to the circulation pits and gasoline passes overhead, to be washed by means of mixing with water in an orifice-fitted line. After settlement in a second vertical tank, refined spirit flows to storage.

By this method the mercaptan content of the spirit is reduced to approximately 0·025 per cent. by weight. The lime employed is produced in the refinery by the burning of shells in a simple form of kiln, approximately 1 kilo of slaked lime being required per cubic metre of gasoline. Originally caustic soda was used for this final treatment, but investigation showed that lime could be substituted for caustic with considerable economy and with no appreciable difference in quality of the finished gasoline. The actual saving entailed is about $0·30 (Argentine) per cubic metre of treated spirit.

The author wishes to express his thanks to the Compañía Ferrocarrilera de Petroleo for permission to publish this contribution, to Mr. O. C. Elvins for data concerning the earlier cracking stocks, and to the Field Manager, Mr. E. P. Senior, for valuable suggestions.

TWO METHODS FOR THE ESTIMATION OF THE POROSITY OF LIMESTONE.*

By W. H. Thomas, A.R.S.M. (Member), R. A. E. Chisholm, B.Sc. (Student Member), and A. B. Cameron, B.Sc. (Student Member).

Introduction.

Modern methods of petroleum production and an ever-present desire to produce oil economically with a minimum of wastage have tended in recent years to focus attention on the reservoirs from which oil is derived. In particular it is desired to know under what conditions the oil is held below ground and what are the physical properties of the reservoir which control the flow of oil to the bottom of the well.

In this connection the property of porosity is of paramount importance and its measurement has been the subject of a vast amount of work. Porosity has been stated (1) to be " that property of a solid which makes possible the storage of fluids within itself or, in other words, it is a measure of the fluid capacity of a solid." It is necessary, however, to differentiate between total or absolute porosity and effective porosity, the difference between these being a measure of the closed pores.

A review of the very complete bibliography given in a paper by Fancher, Lewes and Barnes † indicates that whereas oil-sands have received a great deal of attention, few references have been made to the estimation of the porosity of oil-producing limestone strata. The two cases are somewhat different, particularly in respect to the type and disposition of the pores. With oil-sands, the pores are mainly the open spaces between the sand grains, whereas with limestone the pore space consists to a large extent of irregularly-shaped voids varying in size from very fine capillaries to large fissures. The nature of this difference between the pore spaces of oil-sands and those of limestone necessitates certain modifications to the methods which have proved to be suitable for the estimation of the porosity of oil-sands.

It should be realized, nevertheless, that during drilling through or into productive limestone strata, it is almost impossible to estimate the size and volume of the largest pores, that is to say, the fissures.

A core sample will contain only the smaller fissures, for the core will obviously be broken at each normal-sized fissure. Knowledge of the porosity of limestone samples even as large as six-inch cores, therefore, does not give information of the same value as would be obtained from a study of an oil-bearing sand.

In spite of this, however, the necessity for a means for estimating the porosity of limestones still exists, particularly in cases where it is desired

* Paper received Jan. 14th, 1935.—A communication from the Anglo-Persian Oil Company's Research Department, Sunbury-on-Thames.

† G. H. Fancher, J. A. Lewes, and K. B. Barnes, Penn. State Coll. Bull. No. 12, May 1933.

to estimate the potential production from a given area or field, due consideration being given to permeability, pressure reduction, etc.

In the present paper, details are given of two methods which have been found satisfactory for estimating the effective porosity of limestone reservoir rocks. The first of these, a " pyknometer method," consists in measuring by a weighing procedure the volume of liquid capable of being absorbed by a turned cylinder of the limestone of known volume. The second, a " core method," has been designed to enable the porosity of limestone cores to be

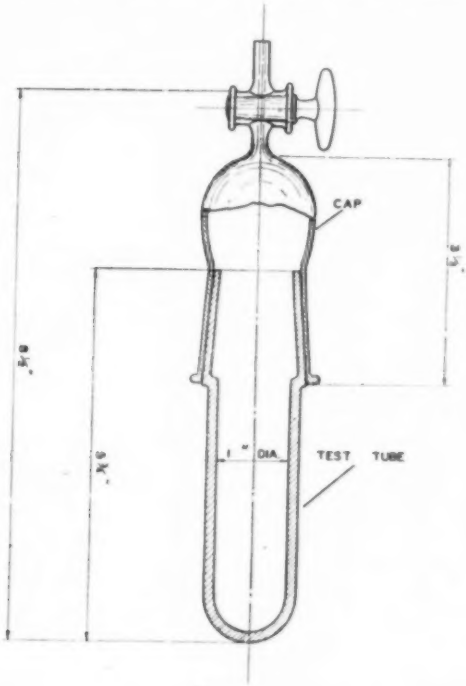


FIG. 1.

determined directly by means of measurements of the reduction of pressure consequent upon releasing a known quantity of compressed air into the core of which the volume is known.

THE PYKNOMETER METHOD.

Apparatus.—The apparatus required for this method is shown diagrammatically in Fig. 1. It consists of a stout glass tube closed at one end and fitted at the other with a cap by means of a well-fitting ground-glass joint. The cap is provided with a well-ground glass tap, and the tube is of such a size as to accommodate a turned cylinder of limestone one inch in diameter and six inches long. Specimens of this size may be prepared from

the length of practically any core and horizontally from those of six inches diameter and upwards.

Preparation of Sample.—The specimen should be accurately turned in a lathe to the form of a true cylinder, using a diamond tool for preference, as the normal type of hard steel tool is blunted very easily with even the softer types of limestone. Provided that the cylinder is true, its volume may be determined accurately by mensuration. The cylinder is prepared by first being dried in an oven at 105° C., and then its content of organic matter is removed by prolonged (*circa* eight hours) extraction with a suitable solvent in a Soxhlet apparatus. The specimen is again dried at 105° C. and stored in a desiccator until required. It is important to handle the turned specimen with care in order to avoid any chipping of the sample.

Method.—As a preliminary, it is necessary to determine, by means of the normal pyknometer technique, the volume of the apparatus at a convenient laboratory temperature, the latter being then used for all subsequent determinations of porosity. It should be stressed, however, that it is essential to use exactly the same quantity of stop-cock lubricant for the ground-glass joint each time the apparatus is assembled, otherwise the volume of the apparatus will vary according to the amount of lubricant used.

The prepared cylinder of limestone of known volume previously freed from moisture and organic matter is placed in the glass tube and the cap fitted in place with the standardized quantity of lubricant on the ground-glass joint. The apparatus with its contents is then weighed (w_1) with the tap open to the atmosphere. The tube is next immersed in a glycerine bath at 110° C., without allowing the glycerine to come into contact with the ground-glass joint and evacuated to as high a vacuum as possible.

The subsequent steps are to close the tap, to remove the connection to the vacuum pump and to invert the apparatus, bringing the tube of the tap below the surface of pure recrystallized benzene contained in a suitable vessel. The tap is opened and the benzene passes into the apparatus, filling the free space and the pores of the limestone. The apparatus with its contents is reinverted, cooled to the temperature of calibration and filled up to the calibration mark with benzene. The whole is then weighed (w_2) with the tap open and the percentage porosity determined, using the equation :—

$$\text{Percentage Porosity} = \frac{\frac{1}{d}(w_2 - w_1) + b - c}{b} \times 100$$

where d = density of the benzene at the temperature of calibration;
w_1 = weight of apparatus + sample (gms.);
w_2 = weight of apparatus containing sample and filled with benzene (gms.);
b = volume of limestone cylinder;
c = volume of the apparatus.

The Core Method.

This method is the same in principle as that described by Lindsley,* the porosity of a limestone core being determined by measurement of the fall

* B. E. Lindsley, U.S. Bur. Mines, Dec. 1924.

in pressure when a known quantity of compressed air is expanded into a vessel of known volume containing the core. Knowing the volume of the apparatus and of the core, the porosity of the sample may be calculated by application of the gas laws.

The apparatus developed for this method is shown diagrammatically in Fig. 2. It may be constructed of steel or bronze and consists essentially of

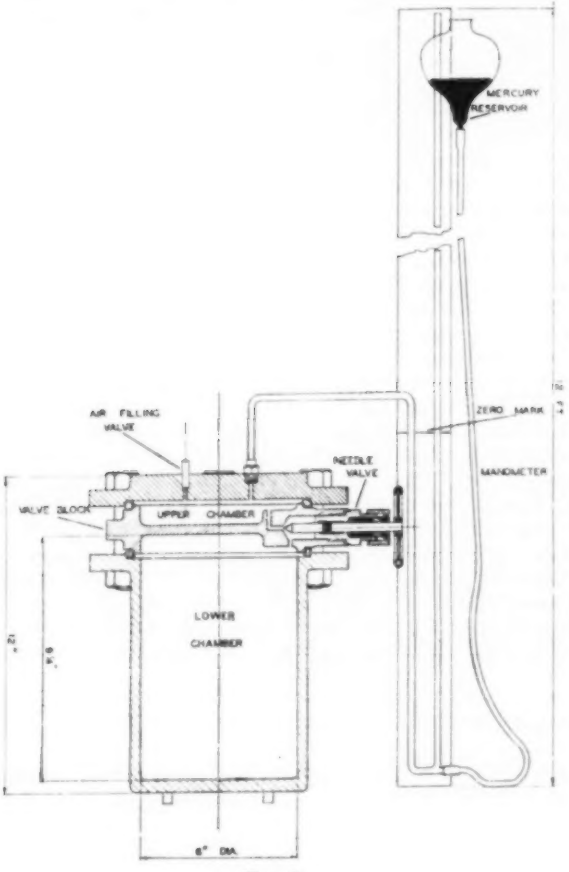


FIG. 2.

two chambers separated by a combined valve block and diaphragm, the function of the latter being to separate the two chambers. The upper of these is for the reception of a charge of air under pressure, while the latter is for containing a portion of an unbroken limestone core (*e.g.* 5½ in. dia. and 9 in. long). The two sections of the apparatus are made gas-tight by means of rubber rings of circular cross section placed between each of the chambers

and the valve diaphragm, but as the cross section of the rings is easily distorted, it is important that the distance between each section be kept constant, preferably by tightening down the nuts against hardened steel gauges or distance pieces. If this precaution is not observed the volumes of the chambers will vary according to the degree of compression of the rubber rings obtained on closing the apparatus.

The volume of the upper chamber is such that, on expansion of the compressed air into the lower vessel containing the core, the fall in pressure is equivalent to about half the original pressure.

The valve controlling the expansion of the compressed air into the lower chamber is provided with a stem fitted with two seatings; the one on the front end of the stem is for closing the air passage connecting the two chambers, and the other at the handle-end of the stem is for preventing leakage of air past the gland packing when the valve is fully opened.

Air pressures are determined by means of a constant-volume mercury manometer of such a height that pressures up to forty-five lb. per square inch may be measured in terms of inches of mercury to the nearest thirty-second of an inch. Compression of air into the upper vessel is effected by means of an ordinary tyre pump delivering through a Schrader valve fitted in the top face of the upper chamber.

As a preliminary, it is necessary to determine accurately the volumes of the two chambers at some convenient laboratory calibration temperature. This may be done either by direct measurement of the volume of liquid required to fill each of the chambers, or by filling each chamber separately with air at a known pressure and then releasing the air into an apparatus suitable for measuring its volume. Application of Boyle's law to the volumes and pressures recorded enables the volumes of the vessels to be calculated.

Preparation of Sample.—Core samples invariably contain quite appreciable amounts of oil and water and these must be entirely removed before estimations of porosity can be carried out. This removal of liquid material from the pores of the core constitutes the chief disadvantage of the method, owing to the prolonged extraction time which is frequently necessary for the complete removal of oil and water.

Moisture may be removed by maintaining the sample at 105° C. for a few hours, while oil or bitumen may be extracted by means of boiling benzene, carbon tetrachloride, carbon disulphide, etc.

A suitable Soxhlet type of metal extraction apparatus is illustrated in Fig. 3. A core sample of average porosity will necessitate at least twenty-four hours' continuous extraction with solvent in order to ensure complete removal of oil. The only satisfactory means for determining whether the core is oil-free is to determine the porosity of the sample, then to extract for a further twenty-four hours and to follow this by a second porosity determination. If the latter gives appreciably higher results, it would obviously be desirable to continue the extraction for a further period. However, when a number of core samples are to be dealt with, the use of a battery of extractors reduces the disadvantage of prolonged extraction time.

Method.—After extraction, the core is freed from solvent by the application of reduced pressure at 105° C., cooled and placed in the lower chamber of the porosimeter, the free space being filled with fine, dry, water-washed sand. The upper chamber and valve block are then assembled, taking care

that the distance between each section is the same as that adopted for the calibration. The apparatus, with the expansion valve and air-charging valve both open, is connected to the constant-volume manometer and the level of the mercury brought to the zero mark by adjustment of the height of the mercury reservoir. The valves are next closed, air is pumped into the upper chamber, the mercury level is brought back to zero and the reading

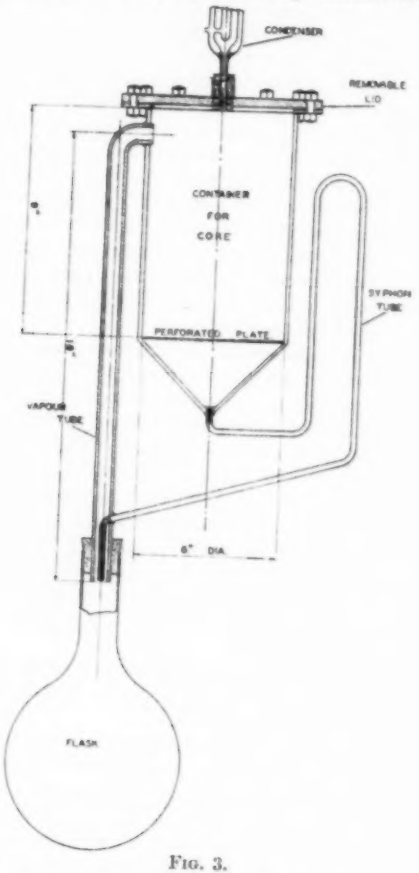


FIG. 3.

of the manometer noted. The expansion valve is now opened and the air allowed to expand into the lower chamber. After no further alteration in pressure is apparent (5–20 mins.) the mercury is again adjusted to zero and the final pressure is read.

The next steps are to remove the core from the lower chamber, leaving the sand, to reassemble the apparatus and to repeat the procedure given above. This second reading enables the volume of the free air space to be determined.

Finally, the volume of the core is obtained by immersing the sample, previously coated with a thin film of a beeswax and paraffin-wax mixture, in water and measuring the displacement of water. A simple type of volumeter may easily be constructed for this purpose.

For the calculation of percentage porosity, the following equation derived from the gas laws is used :—

$$V_1 = \frac{P_1 - P_2}{P_2} \times V_2$$

where V_1 is the volume of air space in the lower chamber;

V_2 „ „ „ upper chamber;

P_1 „ pressure before expansion of air from the upper to the lower chamber;

P_2 „ pressure after expansion of air from the upper to the lower chamber.

The equation enables the following to be calculated :—

(1) The volume of total air space in the lower chamber with core and sand in place $= X$ ml.

(2) The volume of total air space in the lower chamber with the sand in place $= Y$ ml.

$Y - X$ therefore denotes the volume of the core excluding its pores and Z ml. may be taken to represent the volume of the core including its pores, Z being determined by water displacement.

Thus, the volume of the pores is $Z - (Y - X)$, and the percentage porosity is equal to

$$\frac{Z - (Y - X) \times 100}{Z}.$$

Comparison of the Two Methods.

The two methods described in the foregoing have been compared, using a series of limestone cores, cylinders of limestone for the Pyknometer method being turned from the cores after the operation of the Core method. The results are tabulated below and figures for Total Porosity are given for comparison purposes. Total porosity was determined by a simple calculation involving a knowledge of the densities of the sample as a solid and as a fine powder.

Table I.

Sample.	Porosity determined by Pyknometer Method, %.	Porosity determined by Core Method, %.	Total Porosity, %.
1	0·5	0·3	1·3
2	7·5	7·3	7·9
3	13·5	14·5	15·3
4	17·0	20·1	21·0
Accuracy of determination	±0·5	±1·0	—

It will be seen from the above that, for the samples examined, both methods yield results which are appreciably lower than those of total porosity. The differences may be accounted for by the presence in the solid samples of closed pores which are only opened up when the sample is ground to a powder. With samples 1 and 2 the results by both methods are practically identical, but for samples 3 and 4 the Core method gives the higher results of the two, due presumably to the presence in the core of large pores. The latter are invariably not included in the Pyknometer sample, which is selected to be as homogeneous as possible in order to facilitate turning.

Below are given details of the time taken for the operation of each method :—

TABLE II.

	Pyknometer Method.	Core Method.
Extraction of moisture and organic matter	2 hours	24 hours (min.)
Removal of solvent and cooling . .	½ hour	2 „ „
Determination of porosity . . .	½ „	2 „ „
Turning of cylinder	4 hours (max.)	—
Determination of volume of sample . .	—	½ hour
Total time required	7 hours	28½ hours (min.)

The nature of the manipulation of the Pyknometer method makes it the more repeatable of the two, and if this be considered in conjunction with the shorter time required for its operation and the relatively low cost of the apparatus involved, the Pyknometer method is the better for those cases where normal laboratory equipment and a lathe are available.

The Core method, on the other hand, gives results which, although of lower accuracy, approximate more nearly to the true porosity of the sample. In addition, this method does not require costly laboratory adjuncts such as a vacuum pump, lathe and analytical balance, and could be operated satisfactorily in the average field laboratory.

MEASUREMENT OF PORE SIZE.

A knowledge of the percentage porosity of a limestone core by no means characterizes all those physical properties of the sample which would affect or control the recovery of oil. To the production engineer measurements of permeability and pore size are of equal importance to a knowledge of porosity. It is not proposed to deal with permeability here, and in any case it has been covered very extensively by Fancher, Lewes and Barnes (*loc. cit.*). With regard to the measurement of pore size, however, the authors are indebted to Mr. Pickering of the Surrey County Council for details of a procedure which he has found to be suitable for the examination of the pore spaces of igneous rocks. The procedure has been successfully applied to limestone samples and consists essentially of the impregnation of a prepared surface of limestone with Bakelite coloured with an intense dye such as Methyl Violet. On grinding off the excess Bakelite, the pores are seen as highly-coloured threads and spaces which may be measured by means of a microscope fitted with an eyepiece micrometer.

Method.—A small piece of limestone (three-quarters of an inch square and one-eighth of an inch in thickness) is prepared by suitable grinding and then one face is polished on a wet glass plate with a fine grade of carborundum powder or waterproof sandpaper. The specimen is now denuded of its oil content by extraction with boiling benzene and dried. The next stage is to heat the sample on a hot plate, with the polished surface uppermost, to a temperature of about 130–150° C., and then to place on the prepared surface sufficient highly-coloured Bakelite varnish to cover it completely.

The Bakelite enters the pores and on being "cured" by heating provides a hard filling which can be ground and polished. Gentle heating is continued until the Bakelite has hardened, after which the sample is cooled and the excess Bakelite ground off until the original surface is again exposed. After repolishing the impregnated surface, the pores of the limestone are filled with coloured material and are readily discernible by the use of a lens or under the microscope.

In order to avoid damaging the polished impregnated surface, it is advisable to attach a cover glass thereto with Canada balsam. The same material may be used to cement the finished specimen to a microscope slide glass.

For the examination of the pore spaces of a given sample it would, of course, be necessary to cut at least two specimens each at right angles to one another.

The authors are indebted to the Directors of the Anglo-Persian Oil Company for permission to publish this communication.

BIBLIOGRAPHY ON OIL-WELL CEMENT.*

By A. Reid (Associate Member).

There is no lack of authoritative articles on oil-well cementing practice; articles on oil-well cement are scarcer and less satisfying. A working knowledge of cementing principles and practice may be gained from the text-books of Uren,[78] Jeffrey,[39] and Suman,[73] as well as from an excellent paper by Tough.[76] The writings of Case,[15, 16, 17] Parsons,[60] Doherty,[24] Heseldin,[35] Hough,[37] and Pennington [63] deserve mention. Possibly the most up-to-date account is that of Rakestraw and Parsons.[62]

Research on oil-well cement has been largely superficial. Investigations, some of them fairly exhaustive and others of doubtful utility, have mostly been connected with the effects of such physical properties as temperature, pressure and water-content on the setting and hardening properties of cement. It is often difficult to reconcile the results of one worker with those of another, but the differences are possibly explained by differences in the types of cement used and sometimes by the comparative insensitivity of the experimental method. As an example, Uren [78] found that all concentrations of sodium chloride up to 1·0 per cent. increased the setting time of cement set under it. Reid and Evans,[30] on the other hand, showed that progressive small decreases in setting time were obtained with increase in percentage of sodium chloride. Differences in the types of cement used almost certainly account for the discrepancy.†

Further unpublished work on the effect of the CO_3 and SO_4 ions on the setting and hardening of cement has shown that, in the concentrations in which they occur in Burma oil-field waters, these ions have no appreciable deleterious effect on cement. This result was obtained in a study embracing an appreciable range of temperature but at atmospheric pressure. It seems unlikely that the high pressures and temperatures which obtain in the modern deep well will greatly accentuate the action of these ions; the possibility is, however, receiving attention.

Tinnes [75] has considered the possible effects of well waters, as well as gases, oils and formations contacting with the set cement. If his view is rather alarmist this is possibly due to the conditions obtaining in the German oil-fields. Tinnes' article is, however, a very praiseworthy attempt to outline the conditions oil-well cement is called on to meet and repays study. Korepanoff and Muchinsky [45] have also studied the effects of oils and well-waters; their work is known to the author only in the abstract.

In process of placement in the well there is always the possibility that the cement will be contaminated by the mud flush used in drilling. The effect of admixtures of mud flush with the cement grout has been partly investigated by Doherty and Manning [23] among others in the U.S.A., and the author [67] has made a preliminary investigation. Doherty and Manning

* Paper received Jan. 5th, 1935.

† It is interesting to note that Murav'ev [55] also found NaCl to have an accelerating effect; this work is, unfortunately, known to the author only in the abstract.

find that carbonation and mud contamination are so closely associated that the carbon dioxide may be suspected of being dissolved in the mud.

Numerous workers have worked or commented on the effect of temperature on the setting time of cement; the work of Korepanoff and Muchinsky [45, 46] in the U.S.S.R., a translation of which has appeared in the Institution's journal, may be cited. Setting time decreases with rise of temperature and, within certain limits of temperature, a definite relation exists between temperature and initial setting time for a fixed water content of the grout. It should be possible to express this relation mathematically. For deep wells it is essential that the temperature/initial setting time curve should not be steep to allow time for the placement of the cement. At the same time the cement should be as far as possible rapid hardening.

The effect of pressure on the setting of cement has been investigated by Tickell and Wankowski [74] and by Korepanoff and Muchinsky.[46] Using different methods these investigators arrived at different results. Both agree that the percentage reduction in setting time brought about by pressure is proportionately greater for comparatively low pressure, but while Tickell and Wankowski find but little effect as a whole, Korepanoff and Muchinsky find a marked effect. The apparent anomalies appear to be explained by the fact that the Russian investigators apparently used more dilute suspensions; differences in the cements tested may be a partial explanation. The author and his colleagues are at present investigating pressure effects, and the main conclusions so far arrived at may be summarized as follows :—

(i) The effect varies with the type of cement.
(ii) The effects appear to vary at different temperatures.
(iii) The main effect of pressure is one of compaction.

Setting time determinations are to a certain extent crude estimates of the viscosity of the slurry. The slurry reaches its initial set at a certain viscosity, which is determined by studying the penetration of a needle of fixed cross-section acting under a fixed load. Viscosity of a cement slurry is a very important factor in the success of a cement job. Speaking comparatively, the " thinner " the grout for a suitable low water/cement ratio the greater the expectation of a successful issue to a cementation. Incidentally also a " thin " grout considerably eases the burden on the pumps used to place it. In the circumstances it is surprising that little work has been done on the viscosity of cement slurries from the point of view of oil-well use. Viscosity of course has been used by numerous investigators as a means of studying the chemical reactions involved in the setting of cement. The work of Dorsch [25] and of Gessner [32] may be quoted, but their results cannot be applied to oil-well cement as the pastes used had a lower water/cement ratio than is used in oil-well cement slurries. Koyanagi [47] has also worked on the viscosity of cement slurry, but it does not seem to be generally appreciated that cement slurry exhibits anomalous flow and that its resistance to flow should be expressed in terms, not of *one* variable (" viscosity ") but possibly *two* (" yield-value " and " mobility ").* The author has

* To obtain a knowledge of the meaning and application of these terms Bingham's " Fluidity and Plasticity " may be consulted. Scott-Blair has written an interesting article on the application of the modified Bingham equation (*Koll. Zeitschr.*, 1929, **47**, 1, 76), while Ostwald has replied to Scott-Blair's criticisms in the next number of the same journal.

recently been concerned in the design of an apparatus in which it is hoped to be able to find the yield-value and mobility of cement slurries under pressures up to 2000 lb./sq. in. and temperatures up to possibly 180° F.

Some work has been done on additives to cement slurries. The chief additive is calcium chloride, which appears under a number of trade names, "Konset," "Quickset," "Dehydratine," etc. It was formerly the practice to gauge the whole of the cement used in a job with a solution of calcium chloride instead of water. At the present time the tendency is either to dispense with calcium chloride and use a slow-setting, rapid-hardening cement or to use calcium chloride only in the last batch of cement to be mixed. The reason for this is as follows. Calcium chloride accelerates the rate of hardening of cement, a desirable effect, although it does not necessarily increase the ultimate strength; it also decreases the setting time. The last batch of cement to be mixed is placed round the casing shoe, where it is very desirable that it should set fairly soon after placement, rapidly harden and become impermeable. Rapid hardening and quick setting are attained by the use of suitable proportions of calcium chloride, and, since the last batch of cement to be mixed is finally in place a comparatively short time after mixing, the danger of the cement setting before placement is negligible. The Burma practice is to prepare a solution of $CaCl_2$ of specific gravity 1·025, to cool this to about 60° F. and use it to gauge a 45 per cent. to 50 per cent. slurry.

Russian workers [45, 46, 33] have reported on the use of calcium chloride in cement. Since their work is known to the author only in the abstract, detailed comment is not possible. U.S.A. workers also treat of the problem.[13, 43]

Addition of bitumen to cement for oil-well cementing is mentioned by Tinnes (*loc. cit.*). Dyckerhoff [26] discusses bituminized cements, one of which, "Siccofix," cement, recommended by Tinnes, has been tested by the writer. "Siccofix" was found to be a good cement for deep-well cementing, but no more resistant to sulphate or high chloride waters than British cements.

The use of micro-asbestos is referred to by Tinnes. The author is at present carrying out experiments on the addition of micro-asbestos to cement slurries and the indications are that it may prove a useful addition.

It has been suggested that the addition of "Aquagel" or similar bentonitic material to cement slurries is beneficial.[6, 8] Details of the addition of "Aquagel" to building mortars, etc., are given in a handbook issued by the manufacturers of that commodity (Bulletin No. 105 of the Silica Products Corporation of 700 Baltimore Avenue, Kansas City, Missouri), while a paper in the *Oil & Gas Journal* (1932, **31**, 5, 49) describes the use of "Aquagel"-cement mixtures for sealing fissures and cavities encountered in drilling. The addition of such bentonitic materials to cement slurries has a curious effect; the slurry appears more viscous but is actually more readily handled by the pumps—possibly the mobility is increased while the yield value rises. The presence of bentonitic material in the slurry appears to increase the rate of hardening slightly and greatly to enhance the impermeability of the set cement. The author has witnessed the successful use of "Aquagel" in a cement job. A 3 per cent. suspension of Aquagel was

prepared and the cement grouted with this suspension, which had roughly the consistency of thin milk; the cement job was successful.

Average well depths have shown marked increases in the past few years, and as a result the need for slow-setting, rapid-hardening cements, which will set at temperatures up to 200° F., has increased. The possibility of using set-retarding agents has been mentioned, but little work appears to have been done so far.

It has been realized for some time that duration and conditions of storage may have a marked influence on the properties of a cement. Some work appears to have been done, although not in direct relation to oil-well cements. The author has found that cement stored in steel drums alters but little even in the tropics after six months' storage, provided the drums have suffered no damage in transit. Where the drums have been slightly damaged it has been found that a rapid-hardening cement loses the rapid-hardening property after about six months, although the *ultimate* strength attained by a sample of any fixed grout is but little affected. The point is of importance, since rapid hardening is often a desirable property in oil-well cements.

It was the general impression a few years ago, and indeed the opinion is still largely held, that *any* Portland cement would do for oil-well cementing. The author does not subscribe to this view, although he would hardly go as far as Tinnes, who condemns ordinary Portland cement for all well cementations except abandonments. Tinnes discusses the possible use of blast-furnace slag cement, aluminous cement and high-grade Portland cements. He quotes results of experiments by a number of authors on the action of chemical solutions on various types of cement, but appears to forget that some of the results apply to cement pastes and not to cement slurries of oil-well use.

Bates in the U.S.A. is believed to have recommended the use of aluminous cement; the author regrets he has no references to offer. It is not unlikely that local conditions must often decide which type of cement is likely to prove most successful.

The general impression left by a study of oil-well cement literature is that the study devoted to oil-well cements has been much less keen and less far-reaching than that applied to cementing practice. In the words of Rakestraw and Parsons—

> "Summing up, there has been a great improvement in cementing practice since cement was first used to exclude water from oil-wells, but the improvements have practically all been mechanical. It is now time that we investigate the behaviour of the cement itself."

Bibliography.

[1] Alexander, F., "Invasions of Water in Oil Sands," *Oil Bulletin*, Feb. 1927, pp. 161–165.

[2] Anon., "Production and Developments in the Power Field, Navarre County." *U.S. Bur. Mines Bull.* No. 284, pp. 68–73.

[3] Anon., "Multiple Stage Cementing Process Used in East Texas," *Petroleum Engineer*, Dec. 1927, p. 40.

[4] Anon., "Cementing Practice in the California Area," *Oil & Gas Journal*, Dec. 6, 1928, p. 52.

[5] Anon., "Oil Well Cementing Practice," *Oil Age*, July, 1928, pp. 31–32.

[6] Anon., "Aquagel Cement for Oil Wells," *Internat. Zeitschr. fur Bohrtechnik*, 1934, **42** (7/8), 52–54; *Tonind. Ztg.*, 1934, **43**, 58, 522.

[7] Anon., "The Use of Cement in Oil Well Practice," *Oil News*, March 10, 1928.

[8] Anon., "Use of Bentonite Admixtures in Cement," *Oil & Gas Journal*, 1932, **31**, 5, p. 49.

[9] Anon., "Casing String Cemented by Multiple Stage Process," *Oil Weekly*, Sept. 4, 1933, p. 20.

[10] Bachman, L. F., "Service Data for Oil Well Development." A Report circulated by the Pacific Portland Cement Company (1926).

[11] Bachman, L. F., "Discussion of Cements and their Application in Shutting off Water in Oil Wells," *Petroleum World*, Sept. 1927, p. 82.

[12] Balau and Kemmer, "Setting and Hardening of Cements used for Stopping Oil Wells," *Stroitelnuie Materialui* (*Building Materials*), 1930, **2**, 35–41. Abstract in *Chemical Abstracts*, 1931, **25**, 2, 404 [2].

[13] Bell, H. W., and Grimm, M. W., "Tests on Cement and Accelerators," *A.A.P.G. Bulletin*, March 1928, p. 272.

[14] Buhman, E., "Cement for Cementing of Oil Wells, etc." U.S. Pat. No. 1,781,267, Nov. 11, 1931. Abstract in *Chemical Abstracts*, 1931, **25**, 1, 185 [3].

[15] Case, J. S., "Use of Hydraulic Cements in Oil Wells," *Petroleum World*, Aug. 1929.

[16] Case, J. S., "Cementing below Water Strings requires Care and Skill," *Oil Field Engineering*, Aug. 1929, pp. 40–42; Sept. 1929, pp. 40–42; Nov. 1929, p. 40.

[17] Case, J. S., "Cementing and Cementing Projects," *Petroleum Engineering Handbook*, First Edition, 1930.

[18] Czepichevsky, L., "The Use of Cement in Shutting off Water in Oil Wells," *Internat. Zeitschr. Bohrtechnik Erdolbergbau u. Geologie*, 1932, **40**, 5, 39–41. Abstract in *Chemical Abstracts*, 1932, **26**, 16, 4452 [7].

[19] Czielewski, L. S., "On the Use of Cement for Water Shut-offs in Bore-holes," *Internat. Zeitschr. Bohrtechnik Erdolbergbau u. Geologie*, 1932, No. 5.

[20] Dewitt, G. B., "The Art of Oil Well Cementing," *Oil & Gas Journal*, Dec. 6, 1928, p. 126.

[21] Doherty, W. T., and Manning, M., "Cementing Problems on the Gulf Coast," *Oil & Gas Journal*, April 4, 1929, pp. 48–130.

[22] Doherty, W. T., and Manning, M., "Cementing Problems on the Gulf Coast," *Oil & Gas Journal*, 1930, **29**, 16, pp. 30 and 148–150.

[23] Doherty, W. T., and Manning, M., "Drilling Mud Contamination blamed for Coastal Cement Failures," *National Petroleum News*, 1930, Sept. 17.

[24] Doherty, W. T., "Oil Well Cementing in Gulf Coast Area," *A.P.I. Prod. Bull.*, Nov. 1933, No. 212, 60. Abstract in *J. Inst. Petr. Techn.*, 1934, **20**, 126, 215A [4].

[25] Dorsch, E., "Hardening and Corrosion of Cement—III," *Cement*, 1933, **6**, 2, 45.

[26] Dyckerhoff, W., "Cements with Additions of Bitumen," *Tonind. Ztg.*, 1933, **57**, 637–639, 660–662; *idem*, **57**, 57, 600. Abstract in *Chemical Abstracts*, 1934, **28**, 12, 3859 [5].

[27] Dyer, Z. A., "Cementing Oil Wells," U.S. Pat. 1,803,507, April 28, 1931. Abstract in *Chemical Abstracts*, 1931, **25**, 14, 3824 [4].

[28] Erlinghajen, C., Jr., "New Uses of Cement in Mines and Researches on the Suitability of Various Cements for such Uses," *Zeitschr. Kali.*, 1930, Nos. 3, 4, 5, 6, and 7.

[29] Evans, J. R., "Bottom-hole Cementing gives Data on Sizes of Shot Holes," *Oil Field Engineering*, Sept. 1929, pp. 13–15.

[30] Evans, J. T., and Reid, A., "Cements and Well Cementing. Effect of Chlorides on the Setting and Hardening of Cement," *J. Inst. Petr. Techn.*, 1932, **18**, 110, 992–1006.

[31] Ferrari, F., "Behaviour of Special Cements in Sulphate Waters," *Cemento Armato*, 1930, **27**, 3, 25–27; *Building Science Abstracts*, N.S., 1930, **3**, 170; *Chemical Abstracts*, 1930, **24**, 20, 5126 [1].

[32] Gessner, H., "Some Experiments on the Setting of Cement. Part II," *Koll. Zeitschr.*, 1929, **47**, 1, 65.

Grimm, M. W., and Bell, H. W., "Tests on Cement and Accelerators," *vide* Ref. No. 13.

[33] Grodzovskaya, R., and Lutzenko, N., "Accelerators in Cement used in Drilling Oil Wells," *Zerbaid. Heft. Khoz.*, 1932, **2**, 75–81; *British Chemical Abstracts*, B, 1932, Sept. 9, p. 772 [12].

[34] Heiser, A., "Testing of Cements for Oil Wells," *Tonind. Ztg.*, 1932, **56**, 585–586. Abstract in *Chemical Abstracts*, 1932, **26**, 18, 4930 [16].

[35] Heseldin, G., "Drilling and Production Methods in the Greater Seminole Field, Oklahoma, U.S.A.," *J. Inst. Petr. Techn.*, 1928, **14**, 71, 792–795.

[46] Hill, N. B., and Sutton, C. E., "Methods of Shutting off Bottom-hole Water," *Oil & Gas Journal*, April 1928, p. 90.

[47] Hough, J. F., "Certain Fundamental Conditions in Cementing off Water in Wells," *Oil & Gas Journal*, 1927, Dec. 15, p. 85.

[48] Iscu, V., "Shutting off Water in Deep Oil Wells," Bucharest, 1926 (see Tinnes, Ref. No. 75).

[49] Jeffrey, W. H., "Cementing Casing—Shutting off Water," *Deep Well Drilling*, a Text-book, Third Edition, 1931, Chap. XIV, p. 497.

[50] Jones, W. M., "Methods of Testing Water Shut off," Paper read before California District Committee, A.P.I. Division of Production Engineering (date uncertain).

Kemmer and Balau, "Setting and Hardening of Cements used for Stopping Oil Wells," *vide* Ref. No. 12.

[51] King, V. L., "New Cementing Head saves Time on Deep Wells," *Petroleum World*, May 1929, p. 112.

[52] Kinzie, R. A., "How to determine the Weight per Cubic Foot of the Cement Slurry used in Oil Well Work," *Petroleum World*, May 1929, p. 88.

[53] Kirchner, W., "Accelerating Hardening of Cement," U.S. Pat. No. 1,782,471, Nov. 25, 1931. Abstract in *Chemical Abstracts*, 1931, **25**, 2, 392 [14].

[54] Kocharov, S. B., "Cementing Oil Wells," *Heft.*, 1931, **2**, 18, 14–17. Abstract in *Chemical Abstracts*, 1934, **22**, 9, 2868.

[55] Korepanoff, V. N., and Muchinsky, W. K., "Cementation of Oil Wells with the Use of an Accelerator," *Heft. Khoz.*, 1930, **19**, 628–640; *J. Inst. Petr. Techn.*, 1932, **18**, 197–212. Abstract in *Chemical Abstracts*, 1931, **25**, 3470; *idem.*, **27**, 5, 1152 [1].

[56] Korepanoff, V. N., and Muchinsky, W. K., "Cementing Oil Wells with an Accelerator, III," *Heft. Khoz.*, 1931, **20**, 387–400. Abstract in *Chemical Abstracts*, 1933, **27**, 7, 1741 [4].

[57] Koyanagi, K., "Viscosity of Cement Slurry," *Rock Products* (Chicago), 1933, **35**, 18, 30.

[58] Knapp, I. N., "Cementing Oil and Gas Wells. The Plug System," *Trans. A.I.M.E.*, **48** (see Suman, Ref. No. 73).

[59] Lavetzkii, V. E., "Portland Cement for Oil Wells," *Onti-Azneftelzdat*, Baku, 1932, p. 51. Abstract in *Chemical Abstracts*, 1933, **27**, 4, 825 [6].

Lutzenko, N., and Grodzovskaya, R., "Accelerators in Cement used in Drilling Oil Wells," *vide* Ref. No. 33.

[60] Lutzenko, N., and Yaichnikova, E., "Effect of Clay on Cement used in Drilling Oil Wells," *Azerbaid. Heft. Khoz.*, 1932, **31**, 76–79. Abstract in *Chemical Abstracts*, 1932, **25**, 13, 3656 [1].

[61] McDonald, R. R., "Oil Well Cementing Methods and Precautions," *Petroleum Engineer*, Feb. 1931.

Manning, H., and Doherty, W. T., "Cementing Problems on the Gulf Coast," *vide* Ref. No. 21.

Manning, H., and Doherty, W. T., "Cementing Problems on the Gulf Coast," *vide* Ref. No. 22.

Manning, H., and Doherty, W. T., "Drilling Mud Contamination blamed for Coastal Cement Failures," *vide* Ref. No. 33.

[62] Matler, H. A., "Cementing, the Foundation of the Mining Bureau," *Oil Bulletin*, April 1926, pp. 412–414.

Muchinsky, E. K., and Korepanoff, V. N., "Cementation of Oil Wells with the Use of an Accelerator," *vide* Ref. No. 45.

Muchinsky, E. K., and Korepanoff, V. N., "Cementing Oil Wells with an Accelerator, III," *vide* Ref. No. 46.

[63] McCorkindale, C. L., "That Thing called Efficiency," *Oil Bulletin*, Sept. 1929, pp. 917–919.

[64] Mikhura, L. M., "Faulty Cementing of Oil Wells in the Azneft Dist. in 1931," *Heft. Khoz.*, 1932, **23**, 108–109. Abstract in *Chemical Abstracts*, 1933, **27**, 7, 1741 [5].

[65] Murav'ev, I. M., "Effect of Drilling Waters on Hydraulic Cement," *Heft. Khoz.*, 1929, **16**, 835–855.

[66] Nazarov, V. I., "Action of Kerosene on Portland Cement," *Stroitelnuie Materialui*, 1930, 9–10, 31–37. Abstract in *Chemical Abstracts*, 1931, **25**, 13, 3456 [7].

[67] Neelands, A. R., "Some Notes on Water Shut-off" (Discussion of a Paper by Reppoport, G. G.), *J. Inst. Petr. Techn.*, 1925, **2**, 257.

[68] Oberlin, W. A., Victor, and Vietti, "The Reaction of Accelerators in Cementing off Bottom-hole Water," *Field Engineering*, Feb. 1928, pp. 25–28.

[69] Packer, W., "Shutting off Water by Cement and by Pipe Pressure," *Petroleum Zeitschr.*, 1929, **6**.

[60] Parsons, C. P., "Condition of Hole is important in Running Cement Plugs," *Oil Field Engineering*, Dec. 1, 1928, p. 25.
[61] Parsons, C. P., "Control of Water/Cement Ratios in Oil Well Cementing," *Petroleum Engineer*, Oct. 1929.
[62] Parsons, C. P., and Rakestraw, T. H., "Current Oil Well Cementing Practice," *Oil & Gas Journal*, Feb. 5, 1931.
[63] Pennington, H., "Cementing Oil Wells," *Oil Weekly*, Oct. 19, 1928, p. 183.
Rakestraw, T. H., and Parsons, C. P., "Current Oil Well Cementing Practice," *vide* Ref. No. 62.
[64] Power, J., "Use of Cement to Forestall, not to Cure, Well Troubles, is most Profitable," *National Petroleum News*, July 10, 1929, p. 41.
[65] Reid, A., "Hydrated Lime and Diatomaceous Earth (Diatomite) in Oil Well Cement," *J. Inst. Petr. Techn.*, 1921, **17**, 211–224. Abstract in *British Chemical Abstracts*, B, 1931, p. 720 [13].
[66] Reid, A., "A Tentative Specification for Oil Well Cement," *Proc. World Petr. Congress*, London, 1933, **1**, 413–417; *Oil News*, 1933, **34**, 293–298. Abstract in *Chemical Abstracts*, 1934, **28**, 12, 3859 [9].
[67] Reid, A., "Oil-well Cementing. Effect of Mud Admixtures with Cement and Cement Grouts," *J. Inst. Petr. Techn.*, 1932, **18**, 99, 53–56.
Reid, A., and Evans, J. T., "Cements and Well Cementing. Effect of Chlorides on the Setting and Hardening of Cement," *vide* Ref. No. 30.
[68] Robinson, R. S., "What Operators are Doing to Solve Deep Well Cementing Problems," *Petroleum World*, Sept. 1929, pp. 66–70.
[69] Rubel, A. C., "Cementing Practice," *Oil Age*, Jan. 1929, pp. 36–38.
[70] Sawdon, W. A., "Influence of Surface Conditions on Cementing Casing," *Oil Weekly*, Sept. 4, 1933, p. 20.
[71] Shaver, F. J., "Cementing," *J. Inst. Petr. Techn.*, 1929, **15**, 131.
[72] Silberberg, M., "On Micro-Asbestos, an Addition to Cement for Shutting off Water in Bore Holes," *Petroleum Zeitschr.*, 1929, p. 40.
[73] Suman, J. R., "Methods of Shutting off Water," *Petroleum Production Methods* (Second Edition), 1933, Chap. II.
Sutton, C. E., and Hill, H. B., "Methods of Shutting off Bottom-hole Water," *vide* Ref. No. 36.
[74] Tickell, F. G., and Wankowski, V. O., "Oil Well Cements. The Effect of Pressure on their Physical and Mechanical Properties," *Field Engineering*, Sept. 1928, **4**, 3, 16.
[75] Tinnes, A., "Cement and its Physico-chemical Behaviour as Packing for Petroleum Wells," *Petroleum Zeitschr.*, 1933, **22**, 1, 1–11. Abstract in *Chemical Abstracts*, 1933, **27**, 9, 2286 [5].
[76] Tough, F. B., "Methods of Shutting off Water in Oil Well and Gas Wells," *U.S. Bur. Mines Bull.* No. 163.
[77] Uren, L. C., "Various Methods of Testing Portland Cement for Oil-field Purposes," *Oil Field Engineering*, Sept. 1927.
[78] Uren, L. C., "Oil Field Hydrology. Exclusion of Water from Oil and Gas Wells," *Petroleum Production Engineering* (a text-book).
Vietti, Victor, and Oberlin, W. A., "The Reaction of Accelerators in Cementing off Bottom-hole Water," *vide* Ref. No. 58.
Wankowski, V. O., and Tickell, F. G., "Oil Well Cements. The Effect of Pressure on their Physical and Mechanical Properties," *vide* Ref. No. 74.
[79] Wilde, H. B., Jr., "Cementing Problems on the Gulf Coast," *Trans. A.I.M.E.*, New York, Feb. 1930; *Oil Field Engineering*, April 1930.
[80] Williams, N., "New Practices in going through Cavities in Salt Domes reduce Coastal Drilling Costs," *Oil & Gas Journal*, June 23, 1933.
[81] Wright, R. L., "Present Oil Well Cementing Practice," *National Petroleum News*, Dec. 8, 1926.
Yaichnikova, E., and Lutzenko, N., "Effect of Clay on Cement used in Drilling Oil Wells," *vide* Ref. No. 50.
[82] Zavaskii, E., "Cementation of Oil Wells by the Perkins Method," *Azerbaid. Hefl. Khoz.*, 1928, **6–7**, 30–32. Abstract in *Chemical Abstracts*, 1928, **22**, 24, 3983.
[83] Zevada, M. J., "Cement for Cementing the Casing of Petroleum Wells, and for Plugging the Wells," *Bol. Petroleo*, 1927, **24**, 410–412. Abstract in *Chemical Abstracts*, 1928, **22**, 16, 30–40 [4].

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Seventh Annual General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at 8.30 p.m. on Wednesday, 28th November, 1934, at the Apex Club, Fyzabad. Mr. G. H. Scott, B.S., Branch Chairman, presided.

The following paper was presented :

GAS-OIL SEPARATORS.

By J. W. HARDY (Associate Member).

Recent developments in production methods have created a demand for a gas-oil separator whose most important function is reliable complete separation of the gas from the oil so that small changes in gas-oil ratios may be immediately observed and recorded. Separation with the object of providing field gas supply, though still important, has become a secondary consideration compared to the importance of being able to measure the gas produced from the well. The first essential, therefore, in a separator is a reliable liquid seal over the oil outlet. This is obtained by some form of float control valve, which although simple in theory offers various difficulties in working practice.

It is obvious that the valve controlling the fluid outlet will be acted upon by the pressure inside the separator; it must therefore either be a balanced valve, or be actuated by some force great enough to open or close it against the separator pressure. Both methods have inherent disadvantages; the balanced valve is usually a device requiring accurate machining and fine adjustment and does not stand up to abrasive wear caused by sand and wire-drawing of fluid under pressure: the operation of an unbalanced valve against pressure introduces complication of working parts.

The following devices for float-controlled valves have been used by manufacturers :—

(1) A suspended separator having a valve at the bottom which opens when the weight of oil in the separator is sufficient to overcome a balance weight holding the separator on the valve seat (see Fig. 1). This separator is very suitable for dealing with heavy oil carrying much sand in suspension; it will handle almost any quantity of sand and mud without choking. Its disadvantages are, first that it must be swung in a tank above the level of the oil tanks, and second that it is unsuitable for high-pressure separation.

(2) A balanced valve, either bevel-seated or parallel-seated, operated directly by a float (Figs. 2 and 3). Both forms of this valve have serious disadvantages. The bevel-seat type cannot be exactly balanced, as one seat must be larger than the other, and the grinding of two faces to form a tight valve is a long and difficult business. The exactly balanced parallel-

seat type will leak unless it be perfectly ground to fit, and when in use is subject to rapid wear; once worn it cannot be reground but must be renewed.

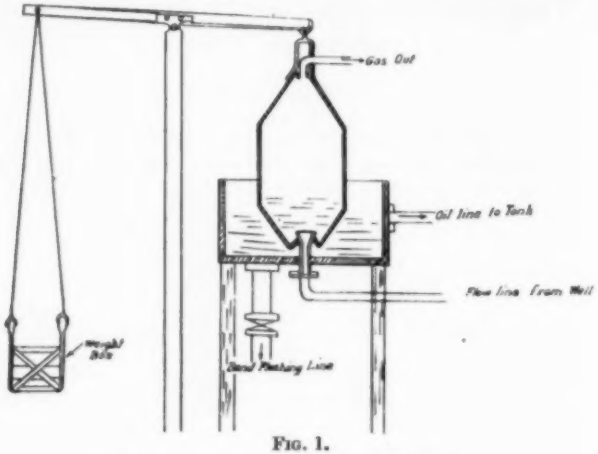


FIG. 1.

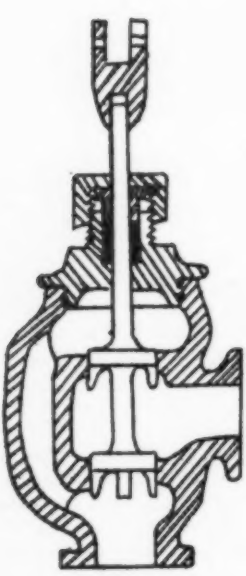


FIG. 2.

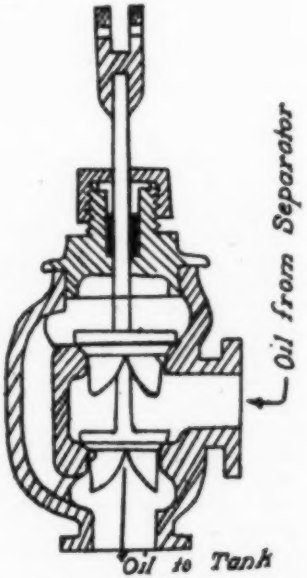


FIG. 3.

(3) The sleeve valve directly operated by a float (Fig. 4). This valve is obviously perfectly balanced as regards pressure, and the large area of surface still in contact between the sleeves when the valve is opening

confines abrasive wear to the edges of the ports, and as long as these edges only are worn the valve can be immediately renovated by resetting. The sleeves should be a perfect ground fit for good results and should be heavy enough to withstand distortion under normal strains. There is considerable friction between the sleeves, so that a large float must be used to operate the

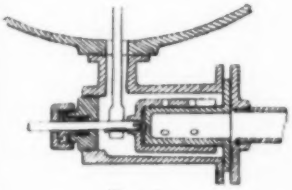


FIG. 4.

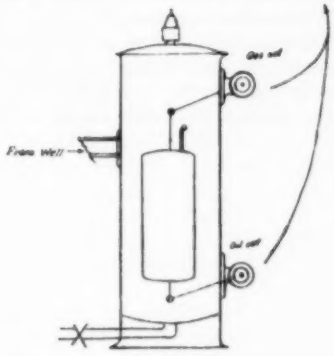


FIG. 5.

valve. For high-pressure separation the float must have a breather hole to equalize the pressure inside and out; this is a disadvantage, since oil foam or mist may find its way into the float and destroy its buoyancy. The sleeve valve has the advantage that it may be coupled to a similar sleeve valve on the gas outlet of the separator so that, as the oil valve opens, the

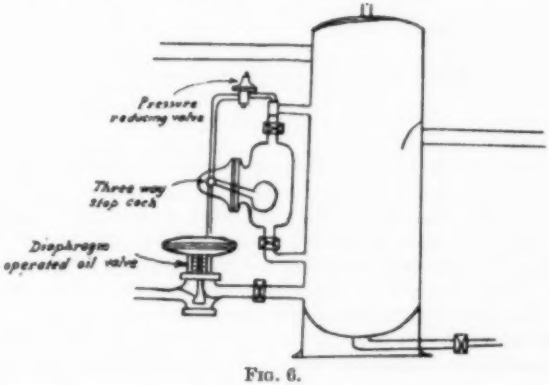


FIG. 6.

gas valve begins to close (Fig. 5). With this device, the separator may be placed below tank level, and the gas pressure will automatically rise till the oil is forced to the tank.

(4) *The slide valve.* A slide valve exactly similar to the D slide valve of a steam engine is used, the separator pressure holding the valve on to the face of the slide. By using a double port slide valve the oil level may be

made to control the gas pressure to obtain the same effect as is obtained by two sleeve valves. For high-pressure separation the slide valve is not very satisfactory because the friction increases with the pressure and a very large float is necessary to operate the valve.

(5) *The pilot-operated valve.* This device simplifies the valve itself but increases the number of working parts required to operate it. A small float is made to operate a valve admitting gas at, say, 10 lb. per sq. inch pressure to a diaphragm which in turn operates the oil valve (Fig. 6). The low-pressure gas supply for the diaphragm is obtained either direct from the separator or through a reducing valve if the separator pressure be too high. Unless a reliable outside source of gas pressure be available, this

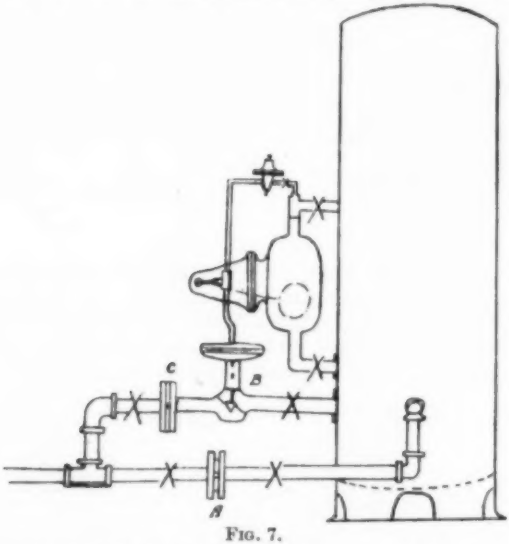


FIG. 7.

device is unworkable if the separator pressure is below, say, 5 lb. per sq. inch. Since a small float only is required to operate the pilot gas valve the float may be housed in a float chamber outside the separator, thus enabling the float to be inspected without disconnecting the separator. The diaphragm valve may be either a semi-balance mushroom valve or a single-seat mushroom valve. By incorporating a lost motion between the float and the pilot valve, the diaphragm valve can be made to operate intermittently so that it is always either full open or tight shut. In this way, destructive wire-drawing action on the valve seat or seats can be eliminated.

For high-pressure separators the pilot-operated valve may be combined with a bean control of the oil level so that the pilot-operated valve deals only with the oil produced in excess of the bean capacity. Protection of the oil valve may be carried a step further by placing a choke in the line beyond it so that there is no differential pressure across the oil valve when it is open. The complete equipment is then as shown in Fig. 7. The cycle of operations

with this equipment is then as follows : the bean or orifice plate at *A* is made (by trial and error) just too small to pass the whole well production at the normal separator pressure. The oil level is therefore slowly rising in the separator. When the float is raised, say, half its travel the valve *B* is opened wide and the orifice plate *C*, whose capacity is about equal to that of *A* but much less than the capacity of the valve *B*, is put in parallel with *A*. The oil level rapidly falls till the float is at the bottom of its travel, when valve *B* closes completely and the cycle begins once more. The valve *B* may be open for, say, two minutes once per hour, and during the time for which it is open there is no differential pressure and only a low velocity across it. In this way, wire-drawing and sand-cutting are eliminated. Since it is essential that the valve *B* should form a dead shut-off when closed, a single seat valve is preferable. In circumstances of widely varying separator pressure or well production, and in the case of small production wells (150 barrels per day and less), the orifice plate at *A* may be shut off, and all the oil passed intermittently through *B* and *C*. Valves should be provided on the connections as shown so that any part of the apparatus may be isolated for inspection.

Summarizing methods of fluid control, it may be said that a sleeve valve operated by a large float in which the pressure is equalized forms the most reliable device and will work both for high and low pressures. It is subject to sand-cutting but may be re-lined when cut, at small expense. For an extensive and lasting programme of high-pressure separation, the combined bean and pilot-operated valve is very efficient, not subject to wear, and cheap to replace or repair.

Assuming a mechanically controlled liquid seal of the oil outlet valve, the next difficulty is the separation of the gas and oil above the liquid level in the body of the separator. The author's experience is that at low pressures (*i.e.* 50 lb. per sq. inch and less) perfect separation always occurs naturally, a clean liquid level is maintained in the separator, and apart from a simple baffle over the oil and gas inlet to divert the stream downwards and a similar baffle over the gas outlet to prevent the passage of possible spray, no other baffling is required. Even with the lowest gas-oil ratios of the order of 200 cu. ft. per barrel, no troubles due to foaming are experienced.

At high pressure, however, there sometimes occurs in the separator a formation of foam which no system of baffles will break down. This condition is usually found at low gas-oil ratios but does not seem to be controlled entirely by that ratio. The following examples will illustrate this.

Well A. Production, 50 barrels per hour; gas-oil ratio, 330 cu. ft. per barrel; tubing pressure, 450 lb. per sq. inch. Separator dimensions, 3 ft. 6 in. diam., 12 ft. high, equipped with two simple inverted cone baffles in the top shielding the gas outlet. Separator pressure, 240 lb. per sq. inch. No proper separation at all was obtained, the whole of the separator appeared to be full of foam so that the gas line was flooded with oil, and much gas was carried along the oil line to the tanks. Above 100 lb. per sq. inch, good separation apparently ceased entirely. After several days the gas-oil ratio increased to 400 cu. ft. per barrel and good separation was obtained at 240 lb. per sq. inch.

Well B. Production, 65 barrels per hour; gas-oil ratio, 250 cu. ft. per barrel; tubing pressure, 500 lb. per sq. inch. Separator 3 ft. 6 in. diam., 15 ft. high, equipped with inside skirt of Kettleman Hills type and mosquito netting baffle across the top below the gas outlet. For the first few days separation could not be obtained at 250 lb. per sq. inch, though 100 lb. per sq. inch gave good results. Later, although the gas ratio scarcely increased, excellent separation was obtained at the higher pressure, but it was found that there was always a layer of foam up to 2 ft. deep above the oil in the separator.

Well C. Production, 67 barrels per hour; tubing pressure, 600 lb. per sq. inch; gas-oil ratio, 190 cu. ft. per barrel. Separator as for Well B but equipped only with simple inverted cone baffles at the top. At 250 lb. per sq. inch perfect separation was obtained two days after the well came in, though there was certainly a deep layer of foam above the oil.

Analysis of conditions in the case of Well B shows that there was entering into the separator a mixture of oil and gas which at 250 lb. per sq. inch contained 15 cu. ft. of gas to every 5·6 cu. ft. of oil. As the skirt deflected the mixture downwards and the gas then had to rise to the gas outlet at the top of the separator, the upward velocity of the gas through the mixture would be :—

$$\frac{65}{60} \times \frac{15}{1{\cdot}75^2\pi} = 1{\cdot}7 \text{ ft. per minute,}$$

and the gas-oil ratio at the separator pressure would be :—

$$\frac{15}{5{\cdot}6} = 2{\cdot}7 \text{ to 1 by volume.}$$

These would certainly be foam conditions according to the Versluys theory, and separation into drops of oil and free gas would be impossible. This seems to show why separation was not obtained in this case, but if that explanation is correct, how can one explain the separation obtained at Well C where the gas-oil ratio was less and the separator pressure the same? There was no skirt in the separator at Well C to deflect the incoming mixture downwards, but as there was not one at Well A either, and separation was *not* obtained there, the presence or absence of the skirt cannot be the deciding factor. The gravity of the oil was very nearly the same in all three cases.

The author has had no opportunity for further experiment and at present is at a loss for an explanation of these apparently conflicting phenomena.

DISCUSSION.

Mr. M. A. ap Rhys Pryce thought Mr. Hardy should be congratulated on choosing a subject for discussion which was generally rather neglected and left to trial and error. As the author pointed out, under modern conditions of production the accurate separation and measurement of gas from oil was very important.

There were one or two points which occurred to him that might be of value to the discussion. First of all he could endorse the author's statement to the effect that, summarizing methods of fluid control, it might be

said that a sleeve valve operated by a float in which the pressure was equalized was best both for high and low pressures, though he would like to modify the statement in that, for high pressure, he did not think an automatic valve alone would last for any length of time if sand was present. His experience had been that no valve of any kind would last long under high-pressure conditions without the assistance of a bean. The system of bean control combined with a dump valve had proved in nearly every field to be the most satisfactory in the matter of separation under high pressure.

Mr. Hardy recommended dumping once per hour or sometimes oftener. He believed that with the assistance of an infinitely variable bean control the dumping frequency could and should be reduced considerably, since the dump valve did not last very long if it was operating too frequently.

The author had raised some interesting points in regard to his examples of Wells A, B and C. He thought they all had had the experience that in separation under high pressure the difficulty was separation of foam.

He did not think he could answer the question entirely in explaining the conflicting phenomena, but he thought it was necessary to consider what foam actually was. It could be briefly described as bubbles of gas surrounded by oil. The stability of foam was dependent on the differential velocity. This was more or less an established fact in the case of a well producing oil and gas moving in the same direction. In the case of a gas trap the oil and gas moved in opposite directions, since the gas was taken out at the top and the oil moved downwards to the oil outlet. Assuming the gas moved upwards with velocity $= V$ and the oil moved downwards with velocity $= U$, then the differential velocity became $V + U$. In order to eliminate the presence of foam, $V + U$ must exceed a certain minimum. In the case of low-pressure separation, where gas was travelling out of the trap at considerable velocity, $V + U$ always exceeded the necessary minimum except with very low gas-oil ratios. With high-pressure separation, however, the velocity of the gas leaving the trap was reduced many times, and $V + U$ was often not of sufficient magnitude to prevent formation of foam. It was clear, however, that if the pressure in the trap was reduced, V (the velocity of the gas) was increased considerably, $V + U$ would similarly be increased and good separation would probably be obtained. Similarly, if the gas-oil ratio increased, $V + U$ would again increase, which again would assist separation. The examples under (A) and (B) seemed to him to be explained by this reasoning.

In the case of Well A, as soon as the gas-oil ratio increased, separation was obtained, and again when the pressure was reduced. In both cases increased velocity of gas was obtained and, therefore, increased differential velocity. In the case of Well B the gas-oil ratio did not increase very much, but it did increase. In the case of Well C the production of that well was well maintained and a high velocity of oil was maintained, which again would give a high value of $V + U$ and, therefore, separation was obtained. In general he suggested that a differential velocity between the gas and the oil was a matter of considerable importance and might be an answer to the problem outlined by the author. In conclusion he would suggest that the inference from such considerations would be to use narrower traps of greater height to ensure greater velocities of oil and gas in leaving the trap. This again might explain the remarkable separa-

tion often obtained with home-made traps constructed of old joints of casing, which had poor control and sometimes no control at all.

With reference to Mr. Hardy's calculations showing the condition in the gas trap of Well B, corresponding to foam conditions according to the Versluys theory, and therefore indicating that separation would be impossible, he would like to point out that the Versluys calculations were based on experiments made with drops of water falling in air and bubbles of air rising in water. Results obtained for gas and oil would certainly differ very considerably, and especially with every different class of oil and gas. For example, Versluys assumed that the maximum differential velocity possible for a foam condition was 8 inches per second. This was based on J. S. Owen's experiments made with air and water. There was little doubt that foams made from gas and oil would be stable at considerably higher differential velocities. In addition, a fundamental factor in the basic Versluys formulas was ϕ, the ratio of gas and oil in the transition period between "foam" and "mist" conditions. This had been arbitrarily assumed to be equal to 1; *i.e.* when more than 50 per cent. of the gas was present, the mixture must be in a "foam" condition. This assumption does not appear tenable, since in practice oil and gas foams are often encountered which would appear to contain anything up to 80 or 90 per cent. gas.

For these reasons he was of the opinion that the Versluys calculations referred to were not applicable in practice.

Mr. G. A. Walling said that the examples cited by the author were interesting examples of what appeared to be conflicting data as regards gas-oil separation. Possibly there might be some other factors to be considered that had not been stated in the three propositions set down. He did not know whether or not the solubility of the gas in the oil was the same in all three cases. He gave an example of his own experience in dealing with a very much lighter oil than the average Trinidad crude. They had found some difficulty in getting separation with a low gas-oil ratio and at a separation pressure of 80 to 90 lb. per square inch. In that case the solubility of the gas in the oil was in the neighbourhood of 80 cu. ft. per barrel for a fairly low separating pressure. He believed that the solubility of the gas in the oil was partly responsible for the degree of efficiency of the separation. They found that the only way they could get away from the foam condition was to put in traps of very much larger capacity and diameter than those which were normally rated as being adequate for efficient separation. In this case an extremely light oil was being handled. He had also come across conditions where they had to use separation pressures of about 200 lb. per square inch in conjunction with a heavier gravity crude with a lower solubility factor, and there again they had to increase the diameter of the traps for low gas-oil ratio wells so as to get efficient separation. Traps had been tried, constructed from 15-inch casing, which were considerably longer than the normal practice, but with poor results.

If possible, a solubility test should be carried out on the oil so that a comparison could be made between the actual amount of gas coming out of the first stage trap and going to the second stage or into the tanks, and

the amount which can be released theoretically from the oil at that pressure. He believed the refining side of the industry could give them some assistance as to correct separator design because it seemed that high-pressure separation was something in the nature of fractionation. Separation of gas from crude was similar to fractionating tower and bubble tower operation. As far as he was able to gather, the lighter the oil the more difficult separation became. He thought the factors to be considered were the gravity of the crude, the constituency of the gas and the relationship of the gas to the oil.

Reviewing the three examples quoted in the paper, there did not appear to be any explanation as to the varying efficiencies obtained from the data supplied. He would like the author to say if the wells were all flowing steadily or whether they showed any variation in the rates of flow. That might throw some light on the matter.

Mr. A. H. Richard said he would like the author to explain the point where he states : " Unless a reliable outside source of gas pressure be available, this device is unworkable if the separator pressure is below, say, 5 lb. per sq. inch." Mr. Richard saw no reason why it should not work below that.

He did not quite agree with the arrangement shown in Fig. 7. He preferred Fig. 6. His main objection was supported by the author's statement in the opening paragraph, that it was essential that there should be a reliable liquid seal over the oil outlet. There was no reliable liquid seal in the arrangement shown in Fig. 7. It was quite likely that the orifice might be too large for varying conditions, that the oil might drain out and allow gas to flow through the oil line.

Mr. K. W. G. Patterson considered that there was another factor other than the differential velocity mentioned by Mr. Rhys Pryce which had some bearing on separation. He believed that the baffling in separators was designed to create centrifugal action and sudden changes in direction of flow when the oil, being heavier, tended to separate out from the gas.

With regard to the practical operation of separators with the dump type valve mentioned in the paper, a number of these separators with which he was familiar had been in service several months without any trouble, with the exception of one valve which had cut out three times. In this case the well was making water, and this was probably the initial cause of the trouble. This valve had proved very difficult to recondition.

It was obviously an advantage to make the intervals between the opening of the valve as long as possible, but the extent to which this could be done was limited by the steadiness of the rate of flow.

Mr. W. G. C. Tomalin said the only remark he had to make was in connection with high-pressure separation where the author talked about pilot-operated valve being combined with bean control. His experience was that the bean control was very necessary. In fact the pilot-operated valve was ruined in a short time unless it was used purely as an adjustment valve.

The other point he would like to make was with regard to the wells quoted. Mr. Rhys Pryce referred to Wells B and C and suggested that the differential velocity would be different in the two cases in a separator. It appeared that the wells' production was more or less the same and the

gas-oil ratio more or less the same. Therefore he did not see why there should be a difference in the differential velocity. He would like to suggest that foaming was due to some physical factor.

Mr. Rhys Pryce, in referring to Dr. Versluys' theory, made a statement that foam could exist to the extent of 90 per cent. gas in the oil and he, the speaker, would suggest that the maximum for a true foam was 76 per cent. or a gas-oil ratio of 2·8 to 1. That was only slightly in excess of the gas-oil ratio which the author gave for Well C in the trap, and he thought that under trap conditions a "foam condition" could not exist and that it would break down.

The author discussed the mechanical side of traps, but in his opening remarks he stated that the great essential of efficient separation was that small changes in gas-oil ratio might be immediately observed and recorded. The only examples he gave them were for separation pressures in the neighbourhood of 250 lb. per sq. in. He thought he was right in assuming that the carry-over of the gas in solution at that pressure would be in the neighbourhood of 200 cu. ft. per barrel of oil and, therefore, he thought the small variation in gas-oil ratio where there was already an error of 60 per cent. was rather negligible. Mr. Tomalin thought the author could have stressed more the point of lowering the gas-trap pressure, and where figures were available, the question of dual and multi-stage separation to provide greater accuracy in gas-oil ratio measurements.

The Chairman said that he was rather surprised that in the discussion no mention had been made as to the economic benefits of multi-stage separation. It was a well-known fact that the amount of gas liberated by an oil varied greatly according as to whether flash separation or differential separation was permitted. By carrying out separation in the field in a number of stages a far greater proportion of the condensable hydrocarbons is retained in solution in the oil. In fields such as Iran, whose location with regard to local markets and shipping points rendered the operation of a casing-head gasoline plant uneconomical, multi-stage separation with its attendant advantages of an enriched crude oil and reduction of the number of pipe lines, appeared to be peculiarly suitable. Even, however, in fields ideally situated for the operation of natural-gasoline plants, the reduction in plant capacity consequent on the smaller throughput of rich gas and tank vapours should render it more economical.

The only other point he wished to raise was with regard to the question of the foam conditions mentioned by the author. It seemed to him that foam formation was largely dependent on the surface tension of the oil, and the stability of the foam on the presence of nuclei of colloidal dimensions.

Foam is in reality an emulsion of gas in oil or vice versa. Taking an analogous form of emulsion, that of oil and water, many oils could not be induced to emulsify in water as long as both were entirely pure, but the small dust particles adsorbed by even momentary exposure to the atmosphere would often be sufficient to allow of the formation of a refractory emulsion on agitation. He suggested, therefore, that many of the anomalies of variation in foam stability with similar gas-oil ratios might be due to variation in surface tension and the presence or absence of minute clay and sand suspensoids in the fluid.

The Author, in reply to Mr. Rhys Pryce regarding the dump valve being cut in the combination of dump valve and bean control, said, the first experience he had of a trap under that control was with a dump valve made up on the spot from a simple 1-inch globe valve with a diaphragm put on the top of it. It was, therefore, a single-seat valve with the one seat ground in tight, and it was put on the separator the wrong way about so that the pressure tended to close the valve, and was, therefore, against the packing and the gland. It opened once every twenty minutes, remaining open about two minutes each time, and worked like that for three months, and at the end of that period it was still in perfect condition. He thought the great trouble in getting the dump valve to function satisfactorily was that the manufacturers put a semi-balanced double-seat valve under the diaphragm, and it was a most difficult thing to grind in such a valve and get a dead seat, while if it leaked at all it very rapidly cut out, no matter whether it opened once an hour or once a day.

With regard to the suggestion that the use of a small-diameter separator of considerable height might obviate foam conditions, he would be willing to support that theory only if it were considered that the foam were formed in the separator. In his opinion, however, the foam was formed in the flow line between the well bean and the separator, and the purpose of the separator was to break down the foam already formed. In that case, a conclusion opposite to that of Mr. Rhys Pryce's would be reached; *i.e.* that the greater the volume and cross-sectional area of the separator, for the longer period would the foam have opportunity to break and the greater area of foam would be exposed to the gas. Also, from a mechanical point of view, supposing any foam to be present in the separator, the greater the upward velocity of the gas the more likely it would be to carry the foam with it in suspension, irrespective of whether the foam were in process of breaking down or not.

If it were assumed that the gas-oil mixture reached the separator in the form of alternate slugs of oil and gas, or as oil mist and free gas, then perhaps a high narrow separator might be successful, but in that case it was difficult to see how a tenacious foam occurred at all, and the ordinary separator would probably work quite as well. In any separator in which gas and oil were present, whether as mist or foam, the only factor causing ultimate separation was the difference in gravity between the oil and the gas, and advantage of this could only be taken by reducing the velocity of the mixture as a whole.

In reply to Mr. Walling the three wells in question all flowed remarkably steadily and they were all more or less in the same horizon and producing from the same sand. He had made no test, but he thought they could take it that the gas and oil were equally soluble in all three cases. He thought, perhaps, in the case of Well B he would adopt the Chairman's explanation, so that for the first two or three days after the well came in the oil was contaminated with mud and sand particles and that might have caused the unusual foam conditions. After several days' production, when the well steadied down and there was no trace of sand present at all, they got perfect separation, though the production of gas and oil still remained almost the same. Mr. Walling also raised the point of being unable to get separation at as low a pressure as 80 lb. per sq. inch. The

author knew of one case where series separation was tried; the oil coming from a 250-lb. separator was led over to a low-pressure separator working at about 10 lb. per sq. in. In the high-pressure separator there was a perfect oil seal so that all the gas coming to the low-pressure separator was dissolved in the oil. On the low-pressure side no separation was obtained, the whole of the low-pressure separator was filled with foam and no readings of the gas were possible. That was why he was unable to make any reply to the suggestion of measurement of solubility of gas in the oil, simply because they were quite unable to measure it. The experiment was not prosecuted and he thought it might have been.

In answer to Mr. Richard he suggested 5 lb. per sq. in. for the pilot-operated valve because 5 lb. per sq. in. was about the average pressure at which the diaphragms that he had been accustomed to were worked. He might have put in a lower pressure than that. In the case of a separator working at low pressure the pressure was frequently unsteady and might fall below the pressure which would operate a diaphragm. He agreed that a pressure of 5 lb. per sq. in. was rather a high limit to put on.

Anent the question of a liquid seal in Fig. 7 the bean or choke at A was found by trial and error. A size was found which was definitely too small to take the amount of oil produced by the well at the separator pressure. They had used most successfully an adjustable bean, but before adjustable beans were available they were using fixed beans in sizes going up by 64ths. He had said beans, but they were really $\frac{3}{16}$-in. plates held between two flanges and drilled with holes of the required size. There was not much cutting of the plates, there was always oil on the gauge glass, and as long as the dump was working periodically they knew there must be an oil seal over the orifice plate.

He thought he had already answered Mr. Patterson's query about the dump valve cutting in the case of water being present. If there was water present the cutting was much more accentuated, but even then he thought a single-seat valve would cure the trouble.

In answer to Mr. Tomalin's comment that he had shown examples working at much too high a pressure, he had used these examples because they were the ones in which they were unable to get separation.

With regard to accuracy of gas-oil ratios the author thought it was possible to observe small changes even when using high pressures. Supposing the separator pressure were steady, the amount of gas leaving the separator in solution in the oil would be the constant amount required to saturate the oil at that pressure. If the well produced more gas with the same amount of oil, the same volume of gas would still leave the separator in solution in the oil, and the extra gas would leave the separator as free gas through the gas outlet and would be shown on the gas-meter chart. If the separator pressure changed, allowance would have to be made for the change in amount of gas required to saturate the oil at the new pressure.

On the motion of the **Chairman** a vote of thanks was accorded the author and to their hosts, the President and Members of the Apex Club, for the use of the building.